FINAL
Technical Report for Surfactant-Enhanced DNAPL Removal at Site 88
Marine Corps Base Camp Lejeune, North Carolina

Prepared

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ABBREVIATIONS AND ACRONYMS

AATDF	The Advanced Applied Technology Demonstration Facility
AFCEE	Air Force Center for Environmental Excellence
AFB	Air Force Base
AFP4	Air Force Plant Four
AQT	aquitard
B	bottom
bgs	below ground surface
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CITT	conservative interwell tracer test
cm	centimeter
cmc	critical micelle concentration
cp	centipoise
cu	cubic
d	day(s)
d_e	effective grain diameter
DE&S	Duke Engineering and Services
DNAPL	dense, nonaqueous-phase liquid
DoD	United States Department of Defense
EPA	Environmental Protection Agency
ESTCP	Environmental Security Technology Certification Program
EX	extraction well
f_{oc}	fraction of sedimentary organic carbon in aquifer material (wt/wt)
ft	foot/feet
gpm	gallons per minute
GS/MS	gas chromatography/mass spectrometry
H	high
HC	hydraulic control well
ID	identification
IFT	interfacial tension
IN	injection well
IPA	isopropyl alcohol
IW	Intermediate well (screened in the aquifer below the surficial aquifer where flooding operations were conducted)
IWTP	industrial wastewater treatment plant

| k | permeability |
| K | hydraulic conductivity |

L	low, liter
LANTDIV	Atlantic Division, Naval Facilities Engineering Command
LNAPL	light non-aqueous phase liquid

m	meter(s)
M	medium, middle
MCB	Marine Corps Base
MCL	maximum contaminant level
md	millidarcies
MEUF	micellar-enhanced ultrafiltration unit
min	minute(s)
MLS	multi-level sampler
MPPE	macroporous polymer extraction
MW	monitoring well
MWR	Morale, Welfare, and Recreation

NAPL	nonaqueous-phase liquid
NCDENR	North Carolina Department of Environment and Natural Resources
NFESC	Naval Facilities Engineering Service Center
NPL	National Priorities List
NRMRL	National Risk Management Research Laboratory
NSFO	Navy Special Fuel Oil

| O&M | operating and maintenance |
| OU | Operable Unit |

P&T	pump and treat
PCB	polychlorinated biphenyl
PCE	tetrachloroethylene
PITT	partitioning interwell tracer test
PO	propylene oxide
POTW	publicly owned treatment works
PPG	polypropylene glycol
PV	pore volume, present value

RAB	Restoration Advisory Board
RCRA	Resource Conservation and Recovery Act
RW	Recovery Well

SCADA	supervisory control and data acquisition system
SDWA	Safe Drinking Water Act
SEAR	surfactant-enhanced aquifer remediation
sec	second(s)
SEE/HPO	steam-enhanced extraction/hydrous pyrolysis oxidation
SERDP	Strategic Environmental Research and Development Program
SPH	six phase heating

T	top
TCA	trichloroethane
TCE	trichloroethylene
TM	trademark
TW	temporary well
UF	ultrafiltration
UIC	underground injection control
USDW	underground source of drinking water
U.S. EPA	United States Environmental Protection Agency
VOC	volatile organic compound
wt%	percent by weight

Section 1.0: INTRODUCTION

1.1   Background Information

Due to the limitations of conventional groundwater remediation technologies, innovative methods have been sought to enhance the removal of recalcitrant compounds such as trichloroethylene (TCE) and tetrachloroethylene (PCE), which are frequently trapped in the subsurface as dense non-aqueous phase liquids (DNAPLs). Surfactant-Enhanced Aquifer Remediation (SEAR) is one such method, which has been adapted from enhanced oil recovery techniques used by the petroleum industry. It involves sweeping a surfactant solution across the DNAPL-contaminated portion of the aquifer. The surfactants accomplish rapid removal of the DNAPL contaminant by greatly increasing its effective aqueous solubility and by reducing the interfacial tension between the DNAPL and water phases. In field demonstrations conducted to date, up to 99% removal efficiencies have been achieved with just three pore volumes of surfactant followed by water flooding (Brown et al., 1999). In a typical remediation scheme, surfactants are used to remediate DNAPL source areas and complement the use of other technologies, such as conventional pump- and -treat systems, for removing the dissolved-phase plumes that are associated with DNAPL source areas.

Currently, simple options for remediating DNAPL source areas are limited. Residual DNAPL in an aquifer acts as a continual source of contamination to the groundwater, and site closure cannot be achieved unless the source is removed. This surfactant-based technology will be more cost-effective than conventional pump-and-treat systems and will provide for a more rapid site cleanup.

1.2   Official U.S. Department of Defense Requirement Statement(s)

Listed in Table 1-1 below are the applicable U.S. Department of Defense (DoD) requirement statements:

Table 1-1. Table of DoD Requirements

Service	Requirement #	Requirement Title	Priority (H,M,L)
Army	1.2 c	Solvents in Groundwater	H
Army	1.2 f	Alternatives to Pump & Treat	H
Air Force	95-T07	Treatment of DNAPLs	H
Navy	1.I.1.g	Improved Treatment of Water Contaminated with Chlorinated Solvents	M

Since SEAR is an enhancement to pump and treat which accomplishes rapid removal of source area DNAPL contamination, it can be readily seen how this technology addresses Army requirement 1.2 f and Air Force requirement 95-T07. Additionally, the DNAPL at the selected demonstration site is a chlorinated solvent; this addresses Army requirement 1.2 c and Navy requirement 1.I.1.g.

By causing DNAPL to be quickly removed from the subsurface, SEAR accomplishes two purposes: it prevents further migration of the DNAPL contamination in the subsurface, and it mitigates a continuing source of contamination to the dissolved-phase plume. Thus, the hazard posed by the remaining subsurface contamination is greatly diminished and site closure is accelerated.

SEAR is intended to remove residual DNAPL as well as free-phase NAPL that is not readily mobile (due to viscous forces) under hydraulic gradients. Free-phase NAPL that flows readily into wells can be economically extracted without surfactants; all efforts should be made to remove any readily mobile free-phase DNAPL prior to surfactant injection to minimize the risks associated with potentially uncontrolled migration of free-phase DNAPL. Similarly, sites with dissolved-phase contamination where no residual or trapped NAPL can be identified may not be suitable for surfactant remediation. While SEAR will tend to lower dissolved-phase contaminant concentrations in the long term by removing the contamination source (i.e., NAPL) that is feeding the groundwater plume, the objective of SEAR is not to bring contaminant concentrations down to drinking water standards. Thus, in an overall site remediation scheme, SEAR will be used in a complementary fashion to other technologies that are designed to treat groundwater plumes.

1.2.1 **How Requirements Were Addressed.** The SEAR demonstration funded by the Environmental Security Technology Certification Program (ESTCP) was conducted to remove a chlorinated hydrocarbon DNAPL present in the subsurface adjacent to a dry-cleaning facility operated by the Marine Corps Base (MCB) Camp Lejeune, North Carolina. The contaminant was tetrachloroethylene or PCE, a common dry-cleaning solvent. Prior to surfactant flooding, free-phase DNAPL removal operations were conducted over a period of about 60 days. During this period, an estimated 30-60 gallons of free-phase DNAPL were removed. Later, during the 143-day SEAR demonstration, approximately 76 gallons of PCE DNAPL were removed from this site as a result of both enhanced solubilization and enhanced mobilization of DNAPL, as observed by both elevated PCE concentrations and increased free-phase DNAPL recovery at the extraction wells compared to observations during free-phase DNAPL removal operations that were conducted prior to surfactant flooding. Total DNAPL removal from the treatment zone was lower than expected due to the presence of low-permeability silty sediments at the base of the DNAPL zone. (The estimated permeability of the basal silt layer ranges from about 5×10^{-5} to 1×10^{-5} cm/sec).

The ESTCP SEAR demonstration treated only a portion of the entire source area. DNAPL mass that was removed from the most permeable zones outside the building is expected to lower PCE concentrations in the dissolved-phase plume. A pump-and-treat system has not yet been installed at Site 88; however, an attempt was made to compare the performance of water flooding alone (conducted for aquifer characterization by partitioning interwell tracers) to water flooding with a surfactant solution (surfactant flooding). During the pre-SEAR control test (i.e., the pre-SEAR partitioning interwell tracer test [PITT]), the PCE concentrations at the most contaminated extraction wells did not exceed the aqueous solubility of PCE (i.e., approximately 240 mg PCE/L). On the other hand, PCE concentrations up to 10,000 mg/L (see MLS-4T in Fig 5-1) were observed during the SEAR demonstration, and increased quantities of free-phase DNAPL were collected at the extraction wells during surfactant flooding; therefore, there is no doubt that surfactant flooding greatly increased the rate of DNAPL removal relative to water flooding.

1.3 **Objectives of the Demonstration**

The objectives of this demonstration were to: (1) validate in-situ surfactant flooding for DNAPL removal; (2) promote the effective use of surfactants for DNAPL removal; (3) demonstrate that

surfactants can be recovered and reused; and 4) show that surfactant recycle can significantly reduce the overall cost of applying surfactants for subsurface remediation.

The surfactant flooding demonstration was conducted at Site 88, the location of the central dry-cleaning facility (Building 25) at the MCB Camp Lejeune, North Carolina (Figure 1-1). At this site, groundwater contamination of the shallow and intermediate aquifers has resulted from the storage and disposal of PCE and Varsol™ dry-cleaning solvents. The dissolved PCE plume in the shallow aquifer at Site 88 is shown in Figure 1-2. The footprint of the demonstration well field was 20 ft by 30 ft, and the DNAPL contaminated zone targeted for remediation was the bottom 5 feet of the shallow aquifer. The total aquifer pore volume treated was approximately 6,600 gallons. Injection and extraction wells were screened across the bottom portion of the shallow aquifer from approximately 15 to 20 ft below ground surface (bgs), which coincided with the depth interval of the DNAPL contaminated zone. Varsol™, present as an LNAPL in the upper portion of the shallow aquifer (8 to 10 ft bgs) was not targeted for remediation. However, some Varsol™ was present as a minor component of the PCE DNAPL and was removed incidentally with the PCE DNAPL.

In addition to the subsurface treatment by SEAR, the ESTCP SEAR demonstration was the first to incorporate aboveground treatment of the SEAR extraction well effluent (i.e., groundwater, surfactant, and DNAPL) by pervaporation and micellar-enhanced ultrafiltration (MEUF) for the objective of surfactant recycle. The recovered groundwater containing surfactant and DNAPL was treated using pervaporation, a nonporous membrane process that removes volatile components such as chlorinated solvents from the water and surfactants. The pervaporation-treated effluent was then sent to an MEUF unit, a porous membrane process that concentrates surfactants primarily in the form of micelles, prior to reinjection. Because chlorinated solvents are the most common DNAPL contaminants at DoD sites, the use of pervaporation for the removal of DNAPL from surfactants is expected to be widely applicable. Recovered surfactants were reinjected to demonstrate the feasibility and acceptability (to regulators) of the surfactant recycle concept.

1.4 Regulatory Issues

The remediation of soil and groundwater contamination at Site 88, MCB Camp Lejeune, NC, is driven at the federal level by the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA), the National Oil and Hazardous Substances Pollution Contingency Plan (NCP) and the Safe Drinking Water Act (SDWA). The regional Environmental Protection Agency (EPA Region IV) administers the cleanup programs established under these federal regulations. However, as a federal agent with a site under the CERCLA program, the Navy has the lead on all cleanup activities at the Base. At the state level, the restoration of soil and groundwater resources is overseen by the North Carolina Department of Environment and Natural Resources (NCDENR). NCDENR cleanup standards are dictated by the North Carolina Administrative Code (NCAC), Title 15A Subchapter 2L, titled "Classifications and Water Quality Standards Applicable to the Groundwaters of North Carolina". Many of the risk-based corrective action (RBCA) groundwater quality standards specified by the State of North Carolina are more stringent than the federal SDWA Maximum Contaminant Levels (MCLs). All parties, i.e., the Navy/Marine Corps, EPA Region IV, and the State of North Carolina, have agreed to use the more stringent state standards for groundwater cleanup at Camp Lejeune.

1.5 Previous Testing of the Technology

The SEAR technology has been previously tested at a number of sites. The most recent surfactant flooding demonstrations performed prior to the ESTCP SEAR demonstration were conducted

at Hill AFB. During 1996, surfactant floods were evaluated for the enhanced removal of a complex NAPL under a Strategic Environmental Research and Development Program (SERDP)-funded project at Operable Unit 1 (OU1), and for removal of a chlorinated solvent DNAPL, consisting primarily of TCE, in an Air Force Center for Environmental Excellence (AFCEE)-funded test at Operable Unit 2 (OU2). The surfactant floods conducted at OU1 were in sheet-pile cells; in one cell a surfactant solubilization test was conducted, while in two cells surfactant mobilization tests were conducted. The resulting DNAPL removal efficiency for these tests, as determined by evaluation of pre- and post-soil coring data was 42% by surfactant solubilization and 92% and 93% by surfactant mobilization (Wood, 2000). The poorer recoveries by surfactant solubilization can be attributed to slower recovery rates effected by solubilization compared to high recovery rates induced by the formation of oil-banks induced by low interfacial tensions. The surfactant flooding demonstration at OU2 for DNAPL remediation was designed as a solubilization test, but due to the low interfacial tension of the surfactant formulation, it very likely was also mobilized DNAPL. It was the first SEAR test where hydraulic control was accomplished without the use of sheet-pile barrier walls for containment of injected fluids. The AFCEE OU2 test accomplished approximately $99 \pm 1\%$ DNAPL removal efficiency (as evaluated by partitioning interwell tracer tests) and recovered > 94% of surfactant as determined by mass balance calculations (Brown et al., 1999). These results were achieved using just 2.4 pore volumes of surfactant solution compared to approximately 9 pore volumes of surfactant flooding and poorer NAPL removal efficiency at OU1. In 1997, another surfactant flood was conducted at OU2 by the Advanced Applied Technology Demonstration Facility (AATDF). This flood was designed to improve the performance of surfactant flooding in hetereogeneous subsurface conditions. This was accomplished by intermittent injection of air to create a surfactant foam that preferentially blocked the higher permeability zones (i.e., temporary occlusion of the larger pores); thus, surfactant was diverted to the lower permeability zones where DNAPL was present. During this test, approximately 97% of the DNAPL was removed, as determined using soil coring and PITT data (Meinardus et al., 1999). While the OU2 surfactant floods were extremely successful, there was the perception that the relatively homogeneous and very permeable soils at the site were particularly suited to SEAR. Therefore, in selecting a site for this ESTCP SEAR demonstration, it was considered necessary to find a more challenging subsurface environment for accomplishing the goal of technology validation.
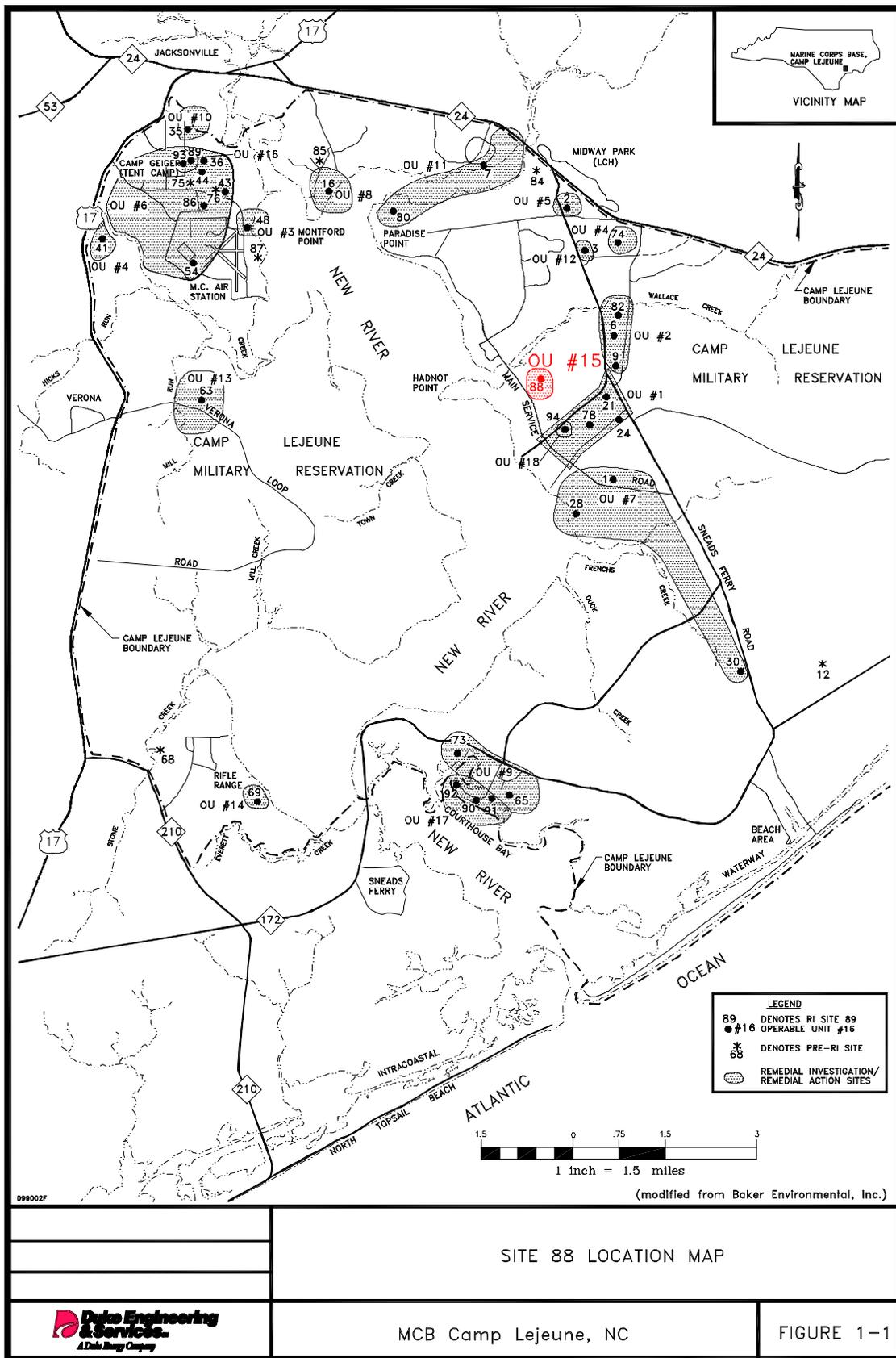
Figure 1-1. Site 88 Location Map
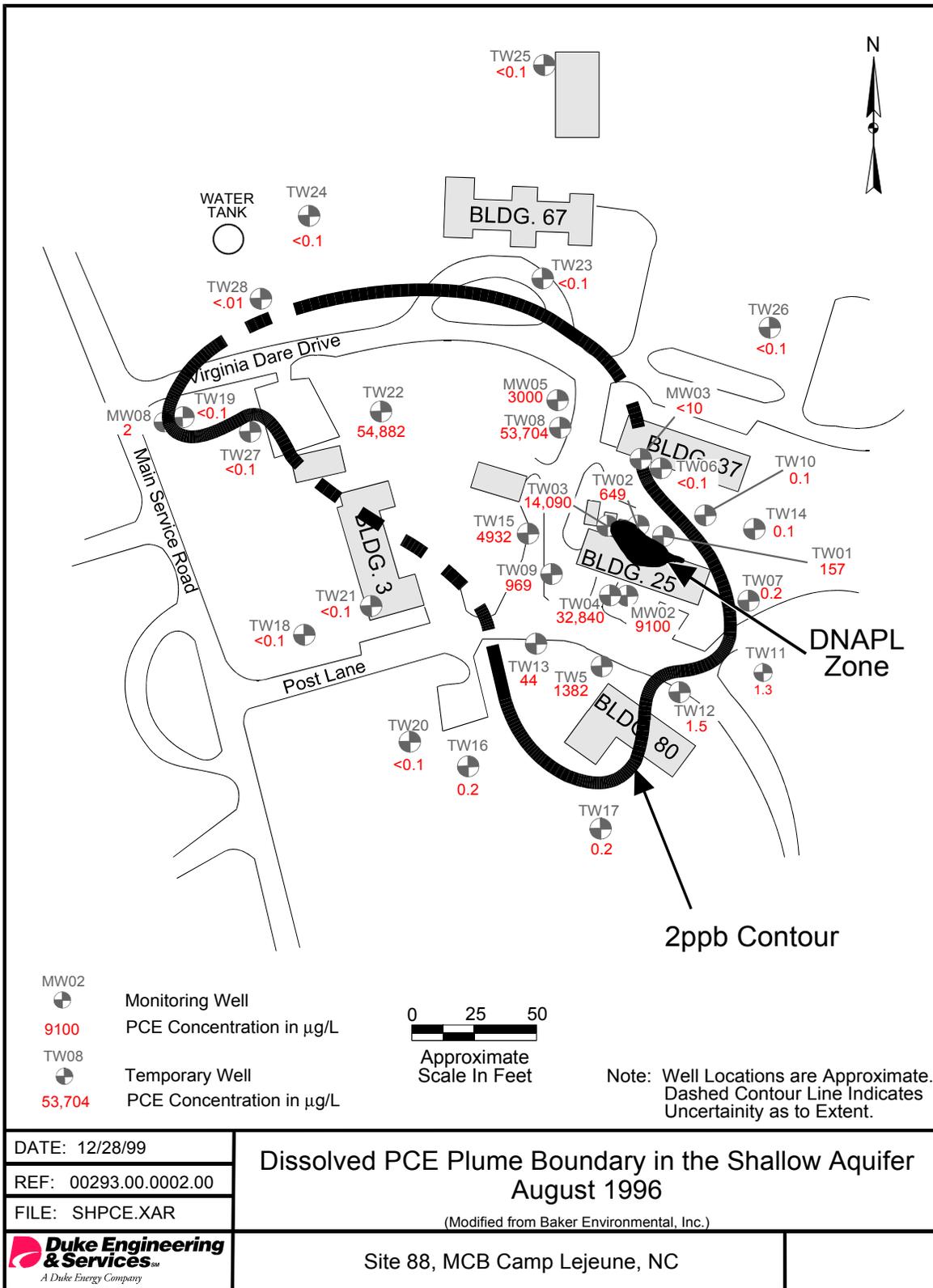
Figure 1-2. Dissolved PCE Plume Boundary in the Shallow Aquifer (August 1996)

Section 2.0: TECHNOLOGY DESCRIPTION

2.1   Introduction

The demonstration of SEAR at Site 88 was conducted from April to August 1999. The demonstration included recovery and recycling of surfactant for reinjection during the surfactant flood. The Naval Facilities Engineering Service Center (NFESC), in Port Hueneme, CA, served as the lead for the project, while the United States Environmental Protection Agency's (U.S. EPA's) National Risk Management Research Laboratory (NRMRL), the University of Texas in Austin, Duke Engineering & Services, and the University of Oklahoma, Norman, were the key technical collaborators on the project. In addition to the funding provided by ESTCP, the Naval Facilities Engineering Command, Atlantic Division (LANTDIV), also contributed substantial funding and logistical support for the DNAPL source zone characterization and SEAR demonstration, as well as provision of utilities and wastewater treatment. The U.S. EPA NRMRL's Sustainable Technology Division in Cincinnati, OH, provided in-kind support for pervaporation unit operation and testing; and the NRMRL's Subsurface Protection and Remediation Division in Ada, OK, provided assistance with DNAPL source zone characterization and performance assessment. This report summarizes the field operations and technical performance of the SEAR technology demonstration that was conducted at MCB Camp Lejeune. The details of the design, implementation, and technical performance assessment of the SEAR demonstration are presented in the SEAR Final Report (DE&S, 2000), which is provided as Appendix G.

2.2   Background and Applications

Surfactants are surface active agents that have two different chemically active parts, a hydrophilic head and a hydrophobic tail. Thus, they exhibit solubility in both water and oil. It is this unique property that allows these agents to greatly increase the solubility of nonaqueous-phase liquids (NAPLs) in water for NAPL removal by enhanced solubilization. If desired, surfactant formulation can also be designed to greatly reduce the interfacial tension (IFT) between the NAPL and water phases such that NAPL removal by enhanced mobilization is achieved. SEAR involves the injection of a surfactant solution consisting of surfactant, electrolyte, cosolvent (i.e., alcohol), and water. Surfactant flooding is followed by water flooding to recover injected chemicals and the solubilized or mobilized NAPL in the aquifer. The extracted fluids are treated aboveground to separate the DNAPL-phase and dissolved-phase contaminants for disposal. The surfactants can be recovered for reinjection if desired. A conceptual illustration of the SEAR process is shown in Figure 2-1. A flowchart showing the SEAR components for the MCB Camp Lejeune demonstration is presented in Figure 2-2. It should be noted that not all the components shown in Figure 2-2 would be used at every site. For example, an alternative scheme, discussed in Section 5.2, may be used if surfactant recovery and reuse are not desired.

When designing a surfactant flood, surfactants are screened for acceptable toxicity and biodegradation characteristics, and minimal sorption to the aquifer mineral surfaces. In most aquifers, mineral surfaces are negatively charged; thus, anionic surfactants are selected because they are composed of negatively charged water-soluble heads, which exhibit minimal sorption. The solubilization behavior, as well as the IFT reduction capacity of most anionic surfactants, is sensitive to the electrolyte concentration. Therefore, anionic surfactants are studied over a wide range of salinities to determine the appropriate electrolyte concentration for phase stability and NAPL solubilization.

If DNAPL mobilization is desired during a surfactant flood, the salinity of the surfactant injectate solution is adjusted to achieve an ultralow IFT. Ultralow IFTs are achieved when the surfactants form a three-phase system (Winsor Type III), which contains excess water and NAPL as well

7

Surfactant Injection

Treatment of Solubilized DNAPL

Extraction of DNAPL and Surfactant
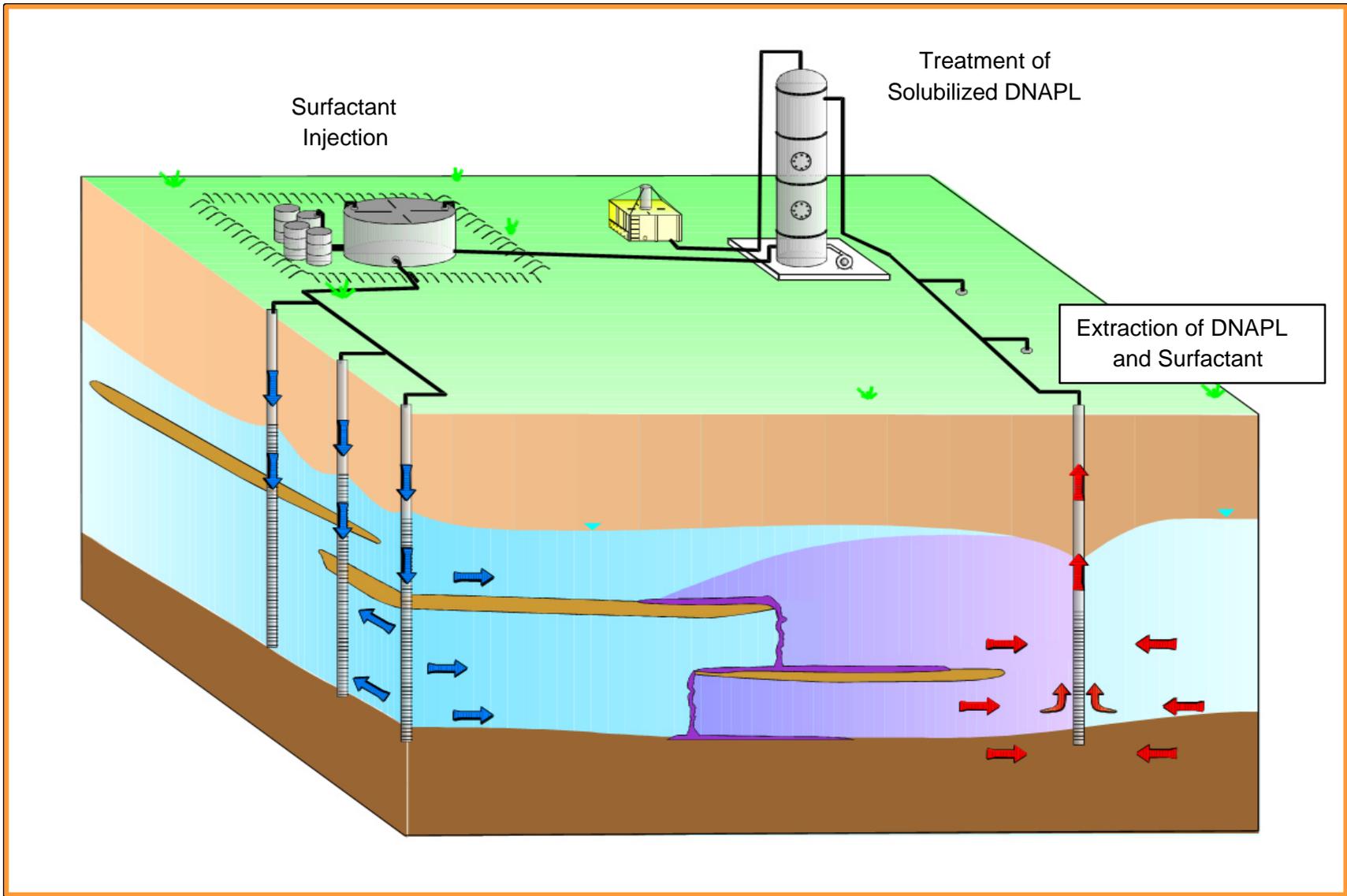
Figure 2-1. Conceptual Picture of SEAR
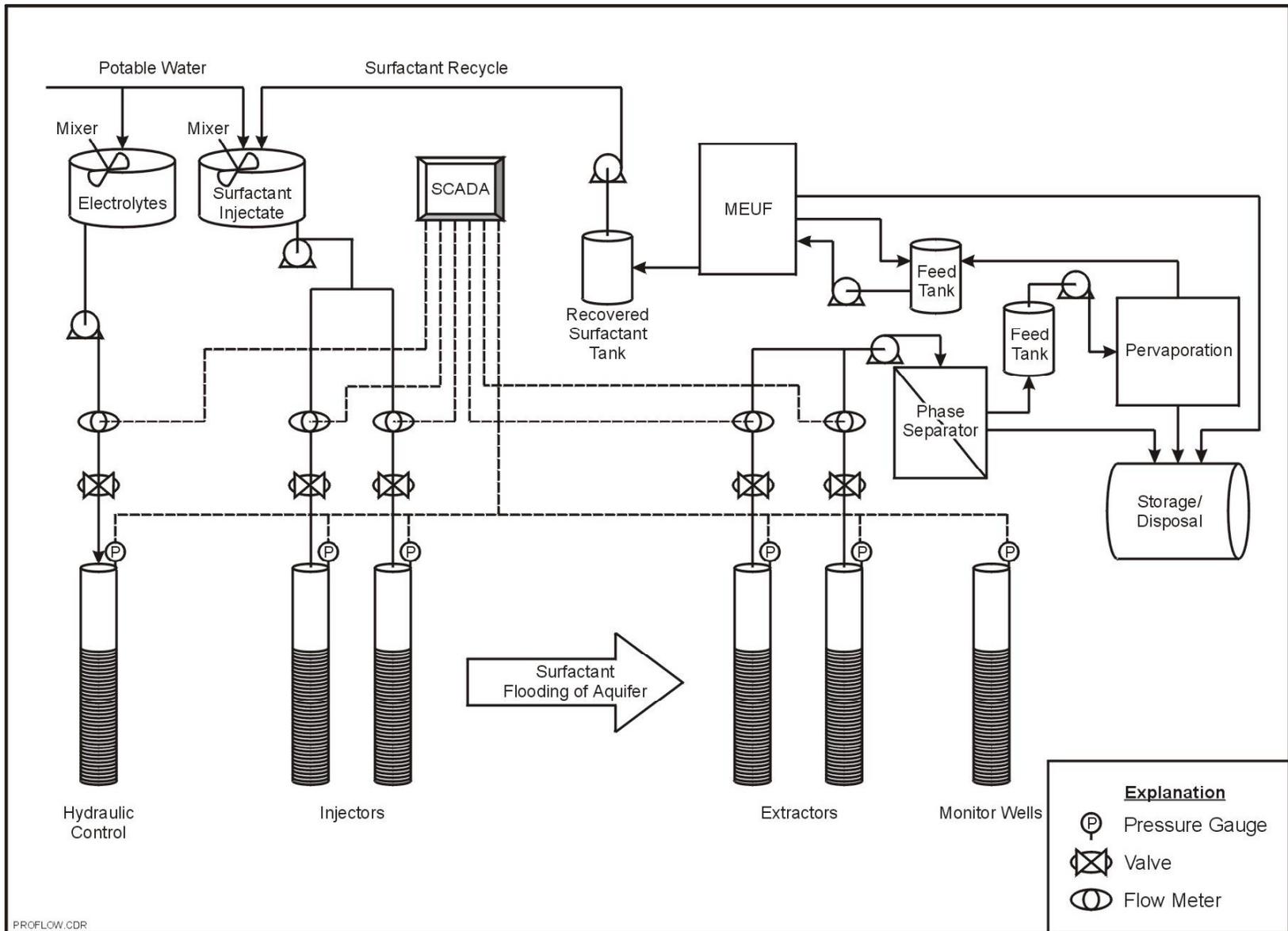
Figure 2-2. Flow Chart for the SEAR Demonstration at Site 88, MCB Camp Lejeune

as a separate middle phase with a large percentage of solubilized NAPL. Because not all surfactants can form Winsor Type III systems, the ability to achieve ultralow IFT may become an additional criteria for surfactant selection. An ultralow IFT system that will result in DNAPL mobilization should not be used if the site does not have an adequate stratigraphic barrier (e.g., aquitard or aquiclude) to prevent downwards DNAPL migration; instead, a solubilization system which minimizes the lowering of IFT should be designed. Typically solubilization systems exhibit Winsor Type I behavior. However, it is also true that low-IFT Winsor Type III systems generally can achieve a much greater solubilization of NAPL, which is more economical; if carefully designed, DNAPL mobilization risks can be mitigated, although not completely eliminated.

Cosolvent is used to improve the solubility of surfactant in water, so that the resulting surfactant-NAPL solution (microemulsion) has an acceptable viscosity (<10 centipoise). High microemulsion viscosities can indicate the formation of surfactant precipitates that will cause pore plugging. The addition of cosolvent also influences the surfactant phase behavior, and its impacts must be examined under a range of system salinities. After surfactants have been evaluated for phase behavior with the site NAPL, soil column studies are performed to evaluate surfactant performance with contaminated site soils. During soil column testing, the difference in pressures between the inlet and outlet of the column is monitored to ensure that there is no pore plugging by surfactant due to the formation of liquid crystals or gels, and/or by ion exchange that mobilizes clay fines. Initial and final DNAPL saturations are measured in the soil column to estimate the mass of DNAPL removed by the surfactant solution and post-surfactant water flooding. The volume of DNAPL mobilized by the surfactant solution, if any, is noted.

Field implementation of SEAR requires the delivery of surfactant to the DNAPL zone via injection wells and the subsequent flow of surfactant through the DNAPL zone, followed by the recovery of surfactant and solubilized DNAPL via extraction wells. The volume of aquifer that is contacted by surfactant as it flows through the subsurface is termed "swept pore volume." The DNAPL zone must be carefully characterized prior to SEAR activities in order to develop a cost-effective SEAR design (e.g., delineating the extent of the DNAPL zone in order to design the surfactant flood to target the appropriate swept pore volume).

Numerical simulations must be conducted to optimize the SEAR design for an efficient sweep of surfactants through the DNAPL zone. A properly designed surfactant flood includes hydraulic control that (a) directs the flow of surfactant through the DNAPL zone and (b) captures the surfactant injectate and solubilized DNAPL at the extraction wells. This control is important for the efficient use of SEAR injectate chemicals, and also to minimize the risk of uncontrolled DNAPL migration beyond the treatment zone. An iterative process of numerical simulations is used to determine the optimum combination of well placement and flowrates of injection, extraction, and hydraulic control wells. A properly implemented SEAR system not only captures the injected fluids and removes DNAPL, but such a forced-gradient flow system also focuses the flow of injectate for a more effective sweep through the targeted DNAPL zones.

Key design criteria for SEAR are provided in Table 2-1.

Table 2-1. Key Design Criteria for SEAR

Design Phase	Key Design Questions
I. Source zone characterization	• Is there any NAPL at the site? • Where is the NAPL located, and what is its approximate volume and extent? • Is the hydraulic conductivity (K) of the aquifer sufficient for the depth of the aquifer and saturated thickness? • Is the aquifer a layered system with a high-permeability contrast between various layers? • Is there a good capillary barrier to downward NAPL migration at the site?
II. Surfactant selection	At groundwater temperature and pH: • Is the surfactant acceptable (e.g., biodegradable) for injection into the aquifer? • Are the surfactant characteristics acceptable for performing enhanced solubilization (Winsor Type I) or mobilization (Winsor Type III), depending on remedial objectives? • Does the surfactant-electrolyte-NAPL system reach equilibrium rapidly (with a stable surfactant phase forming within several hours to 24 hours depending on the anticipated residence time in the aquifer)? • Is the salinity requirement of the system acceptable (because of impurities associated with the bulk salt)? • Is the required cosolvent concentration economically acceptable? • If surfactant regeneration is desired, does the surfactant have the necessary characteristics for filtration? • Do soil column test results confirm that surfactants are as effective in removing NAPL from site soils as predicted from phase behavior testing? • Is there any pressure increase observed during soil column testing (i.e., surfactant sorption and/or pore plugging)?
III. Geosystems model development/Numerical modeling	• Is hydraulic containment being accomplished? • Have subsurface heterogeneities (i.e., variations in aquifer conductivity and DNAPL distribution) been taken into account? • How many pore volumes of surfactant solution are required to remove the desired quantity of NAPL? • Is the duration of water flooding sufficient to accomplish acceptable recovery of injected surfactants and cosolvent (as determined by regulatory requirements)?

SEAR performance objectives will vary from site to site, but are typically evaluated by the following metrics: (1) the final average DNAPL saturation (i.e., the volume percent of the pore space that contains DNAPL); (2) the percent of initial contaminant mass removed (desired value high, e.g., 99% removal); (3) percent mass recovery of the injected chemicals and (4) the risk associated with any DNAPL remaining after treatment as well as the risk reduction accomplished with the DNAPL removal action. With respect to evaluating the effectiveness of DNAPL removal, the final average DNAPL saturation is a more stringent standard than the percent DNAPL recovery, which overlooks the risk of unremoved DNAPL. Usually if the percent recovery of DNAPL is high, the percent recovery of injected chemicals will also be high; however, the opposite is not necessarily true, as poor sweep of contaminated zones may occur even if injected fluids are effectively captured. If the percent recovery of DNAPL is low, evaluation of the percent recovery of injected chemicals may provide some insight as to why this occurred. If poor recovery of injected chemicals is obtained, it is necessary to determine the risk associated with the compounds remaining in the aquifer. In all cases, the risk of unremoved DNAPL and the reduction of risk due to the removed DNAPL should be considered in assessing technology performance. Discussion of the performance objectives established for the ESTCP demonstration is provided in Section 4.1.

Surface treatment of SEAR effluent is complicated primarily by the presence of surfactant, which may cause a foaming problem and provides additional mass transfer resistance to separating the contaminant from groundwater. Application of conventional processes, such as air stripping or steam stripping, may necessitate the addition of antifoam agents or significant operational condition changes in order to control surfactant foaming. The combination of the increased mass transfer resistance and the higher contaminant solubility will need to be considered in designing a treatment process of the appropriate scale for contaminant removal. If alcohol is used in the surfactant formulation, then the alcohol may need to be removed prior to discharging the wastewater to a publicly owned treatment works (POTW) or industrial wastewater treatment plant (IWTP). Due to alcohol's high solubility in water, alcohol removal, if necessary, typically requires a treatment process that is separate from the contaminant removal process. Air stripping, liquid-liquid extraction, and pervaporation are among the potential candidates. However, because of the additional wastewater treatment costs incurred, the most cost-effective solution is to minimize or avoid the use of alcohol in the surfactant formulation whenever possible.

SEAR effluent treatment design may favor an examination of treatment processes that can recycle SEAR chemicals if: (a) on-site facilities are not available for processing the SEAR effluent; (b) the extraction flowrates exceed the available treatment capacity; or (c) chemical injectate costs are greater than recycling costs for a large-scale site. In this ESTCP demonstration, the feasibility and cost benefit of surfactant recovery and reuse was examined. The use of pervaporation as the contaminant removal step avoided the surfactant foaming problem without the addition of antifoam agents, which assisted the recyclability of the surfactant. Pervaporation effluent was sent to an ultrafiltration (UF) unit to remove excess water from the surfactant, i.e., reconcentration of surfactant, prior to reinjection. A general schematic of the pervaporation and MEUF processes is provided in Figure 2-3. The pervaporation treatment train used at Camp Lejeune, which includes two types of pervaporation membrane systems, is shown in Figure 2-4. Alcohol recovery may also be advantageous if significant quantities of alcohol (e.g., > 8 wt%) are used in the surfactant formulation. Alcohol recovery was not an ESTCP demonstration objective; however, it was tested on a small-scale using a second set of pervaporation membranes (U.S. EPA, 2000a).

The surfactant flooding technology is potentially applicable to any type of NAPL that is located in the saturated subsurface. It has been applied to the removal of various chlorinated solvents,
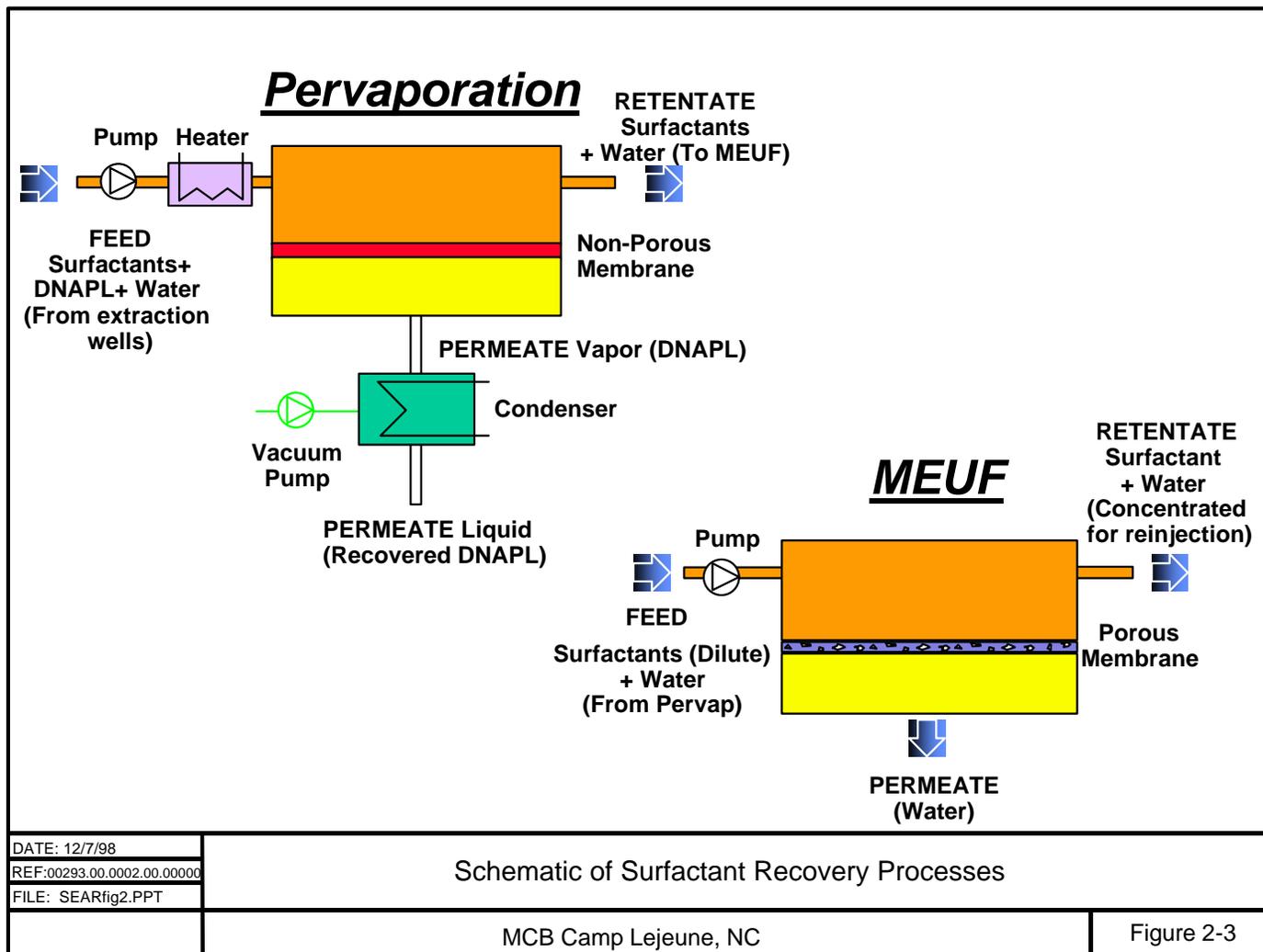
Figure 2-3. Schematic of Surfactant Recovery Processes used at Site 88, MCB Camp Lejeune, NC

From Wells → **Gravity Separator** → **Feed Tank**

DNAPL

Heater

Filters

Condenser

Vent

Vacuum

Wastewater Tanker Truck

Solvent Drums

Water

PCE

PCE-Water Separator

Hollow Fiber

Vibrating

to MEUF

Pervaporation Membranes

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REF: 00293.00.0002.00.00000	**Schematic of Pervaporation System Equipment**
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Site 88, MCB Camp Lejeune, NC	Figure 2-4
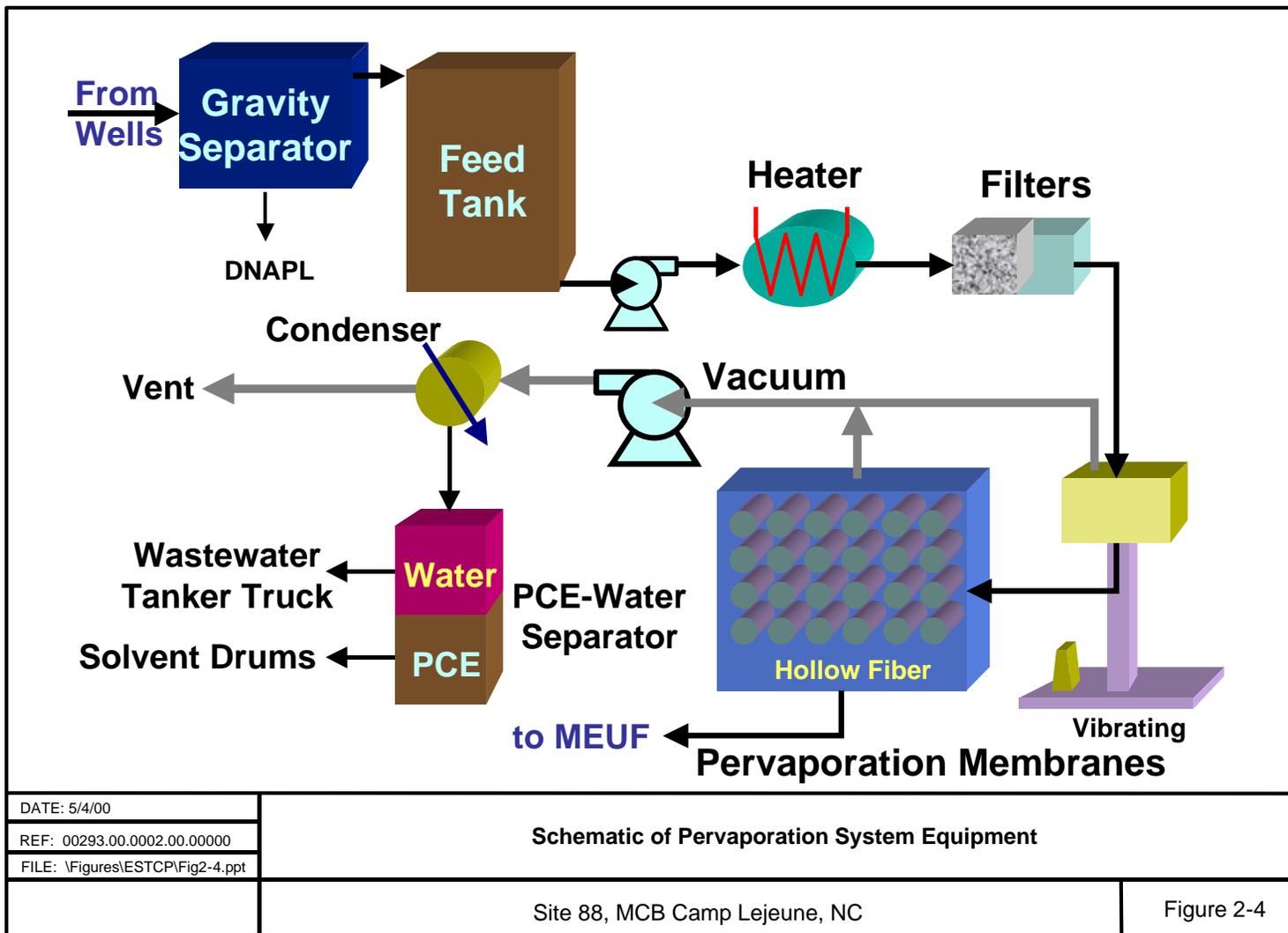
Figure 2-4. Schematic of Pervaporation Treatment Train Used at Site 88, MCB Camp Lejeune, NC

creosote, gasoline, jet fuels, and polychlorinated biphenyls (PCBs) (Lowe et al., 1999). Perhaps the greatest demand for the technology is for the remediation of chlorinated hydrocarbon and polyaromatic hydrocarbon DNAPLs. This demand is due to the prevalence of these DNAPLs as subsurface contaminants, the risk associated with their presence in the subsurface, and the poor performance of conventional remedial technologies that have been developed primarily to address only the dissolved-phase contamination.

2.3   Advantages and Limitations of the Technology

The strengths of the SEAR technology lie in its ability to accomplish NAPL removal quickly and effectively compared to conventional methods for addressing a dissolved-phase plume, such as pump and treat and biodegradation/natural attenuation. Surfactants with high solubilizing capacity (e.g., increases in aqueous solubility by two to three orders of magnitude are quite common), interfacial tension reduction to 0.01-0.001 dynes/cm, suitable viscosity for injection, and low sorption to aquifer sediments are available for a wide variety of chlorinated and nonchlorinated NAPLs. The advantage of SEAR is its ability to overcome the mass transfer limitations that are intrinsic to subsurface NAPL contamination, particularly in the saturated zone. For example, in situ chemical oxidation can only take place in an electrolyte such as groundwater and not in the NAPL itself, which is a nonelectrolyte and cannot transfer electrons easily. Due to the slow dissolution of NAPL in groundwater, the indirect process of NAPL destruction by in situ chemical oxidation is very slow relative to the enhanced mass transfer rates achieved by solubilizing NAPL with surfactants. In addition, the use of oxidants in situ is not applicable to saturated organic contaminants such as trichloroethane (TCA), and also may require monitoring of heat evolution, particularly in the presence of underground utilities. In situ thermal technologies still need to address the issues of adequately contacting the NAPL with heat (e.g., buoyant effects of steam), establishing effective vapor recovery, and the potential requirement for aquifer dewatering which can induce DNAPL drainage into deeper zones. The entire aquifer thickness must be heated to effect NAPL removal. Thus, these competing alternatives may be less efficient than SEAR at NAPL removal, particularly at sites with high NAPL saturations, high permeability aquifers (e.g., high groundwater flux zones are heat thiefs), or calcium carbonate groundwater systems where high temperatures can lead to precipitation of carbonate with subsequent reduction of permeability and potential loss of vapor recovery. Finally, a properly designed surfactant flood, with hydraulic control, imposes a forced hydraulic gradient across the treatment area for a focused sweep of surfactant through the DNAPL zone. Such a flow system has a much greater capability of sweeping heterogeneous zones than remedial technologies that use "passive" injection (i.e., injection without extraction or hydraulic control to direct the flow of chemicals, such as in situ chemical oxidation). Surfactant flooding also has been shown in a number of field trials to be consistently more efficient in DNAPL removal than cosolvent flooding, and typically can accomplish higher DNAPL removal efficiencies with fewer pore volumes of surfactant compared to cosolvent.

Although biological methods most commonly applied to soils with low-level soil and groundwater concentrations are often promoted for NAPL remediation, these methods may be limited by the toxicity of the NAPL and can only be applied to removing contaminant in the dissolved phase due to their nutrient and electrolytic requirements. Furthermore, they are inherently much slower-acting than the more aggressive abiotic remedial technologies.

The SEAR technology requires more extensive source-zone characterization in comparison to conventional dissolved-phase remedial technologies due to the higher liability associated with the potential for unintended mobilization of NAPL. Even though mobilization dominated DNAPL recovery using surfactants is preferred, uncontrolled downward migration of DNAPL is undesirable in aquifers that lack competent capillary barriers, thereby increasing the need for good source-zone characterization.

All aggressive NAPL remediation technologies, such as SEAR and thermal, require greater source zone characterization to ensure safe technology design and cost-effective performance. However, improved source zone characterization is fundamentally required in order to select a remedial technology that is appropriate for the site-specific conditions at a given site. Careful design and execution of a SEAR test is required to ensure hydraulic containment and to prevent any unintended mobilization of NAPL. Once again, costs are associated with this requirement in comparison to technologies that remove DNAPLs much more slowly. Finally, the relatively high cost of SEAR is also due in part to surface treatment costs of extracted wastewater containing surfactant (e.g., with in situ oxidation, contaminants are destroyed in place rather than extracted and treated); the availability of on-site treatment facilities will influence surface treatment costs. The cost of wastewater treatment is one of the reasons surfactant recycling was examined for this ESTCP project.

In consideration of technical limitations, SEAR may be applied at any site with NAPL contamination in the saturated zone where hydraulic control of injected chemicals can be maintained, and where the aquifer is sufficiently permeable. The ESTCP-sponsored SEAR demonstration at MCB Camp Lejeune has attempted to address the current practical lower limit of permeability for SEAR application in shallow groundwater aquifers where strong permeability contrasts exist and using standard extraction well pumps under atmospheric conditions. The advantages and limitations to the application of SEAR are summarized in Table 2-2.

Table 2-2. SEAR Advantages and Limitations

Advantages	Limitations
1. Can address a wide variety of NAPL contaminants	1) Requires extensive source-zone characterization compared to dissolved-phase technologies
2. Overcome mass transfer limitations of dissolved-phase technologies such as pump and treat and in situ chemical oxidation by accomplishing: (a) Orders of magnitude increase in contaminant solubility (b) Low interfacial tensions to mobilize contaminant (c) Efficient contacting of contaminated zones using forced hydraulic gradients	2) Requires competent capillary barrier to avoid downward mobilization of contaminants
3) Rapid removal of NAPL accomplished in weeks and months rather than years	3) Higher liability associated with potential for unintended mobilization of DNAPL
4) Accomplishes higher DNAPL removal efficiencies and uses fewer chemicals than cosolvent flooding	4) High cost of waste treatment relative to a destructive technology such as in-situ chemical oxidation
5) Safe to use near occupied buildings	5) Design and implementation requires personnel with considerable expertise
6) Can be implemented without aquifer dewatering	6) Performance may suffer in shallow, heterogeneous, and low permeability aquifers

2.4   Factors Influencing Cost and Performance

The primary subsurface factors influencing cost and performance are the intrinsic permeability, and the degree of heterogeneity in the aquifer. At one end of the spectrum are the simple sites, where the aquifer permeability is moderate to high (hydraulic conductivity (K) $\geq 10^{-3}$ cm/sec), where there is minor permeability variation, and where hydraulic gradients can be induced for effective surfactant sweep and hydraulic control. At these sites, SEAR implementation and execution is straightforward and the technology has a high chance of success, as defined by the DNAPL removal efficiency and ease of capturing injected fluids. As expected, these also represent the lowest cost sites for implementing SEAR. At the other extreme are the sites with low permeabilities (i.e., $K \leq 10^{-4}$ cm/sec), and/or with a greater degree of aquifer heterogeneity, and/or with high variations in static hydraulic gradients, such as that caused by tidal influence. At such sites, SEAR design is more rigorous and there is higher uncertainty about the result. A high performance surfactant (i.e., high solubilization) with excellent phase stability is necessary under these conditions.

As permeability variations or heterogeneities increase, there is a greater chance for inefficient sweep of the lower permeability zones due to short circuiting through high permeability zones; thus, more pore volumes of surfactant and post-surfactant water flooding may be required for DNAPL removal. Alternatively, if the permeability is sufficient and the appropriate hydraulic gradients can be applied, polymer or foam may be used as a means of mobility control to mitigate flow through the higher permeability zones (i.e., reduce short circuiting) and effect more surfactant flow through the lower permeability zones. This reduces the number of pore volumes and chemical costs required to remediate the lower permeability zones of a heterogeneous aquifer. Since there will always be some heterogeneity in permeability, it is wise to use only surfactant formulations that are very efficient in solubilizing contaminants along with some means of mobility control. At Camp Lejeune, mobility control measures could not be readily implemented due to the combination of shallow conditions and low permeability, which limited both the range of hydraulic gradients that could be imposed as well as the composition of the surfactant formulation. Additionally, implementing surfactant-foam for mobility control places emphasis on a well-foaming surfactant, whereas at Camp Lejeune, the focus was on a low critical micelle concentration (cmc) surfactant that could be recovered using ultrafiltration. The Camp Lejeune demonstration site, with both low bulk hydraulic conductivities and a high permeability contrast (K ranged from approximately 10^{-5} cm/sec to 5×10^{-4} cm/sec) represents one of the most challenging site conditions where SEAR has been implemented.

As mentioned above, a complicating factor at Camp Lejeune was the thin, shallow aquifer, which limited the range of hydraulic gradients that could be imposed on the system between the injection and extraction wells. The limited range of hydraulic gradients that could be imposed across the test zone during the surfactant flood therefore limited the velocity of the surfactant solution sweeping the subsurface between a given injection and extraction well pair. This condition reduced the allowable interwell distances, which necessitated a greater number of wells, and in turn generated a greater number of sampling points. In some instances, the use of more wells can be advantageous, as finer control of gradients over shorter distances can be maintained; however, the existing combination of low permeability and shallow aquifer conditions at Site 88 limited the flexibility for increasing the interwell distance to reduce the total number of wells and the associated well field costs.

Therefore, it is necessary to invest funds to adequately characterize the source zone to identify any potential complicating factors for SEAR design. Even at the "simple" sites, a thorough understanding of the hydrogeology, the DNAPL distribution, and the geochemistry is necessary to accomplish "acceptable" performance that avoids worsening the DNAPL contamination. Once the

subsurface conditions are well characterized, a wellfield configuration of injection, extraction and hydraulic control wells can be properly designed. Numerical modeling can also then be used to accurately design flowrates to allow sufficient contact time of the surfactants with the DNAPL and to provide effective hydraulic capture ($\geq 90\%$)[1] of the injected fluids. Finally, a robust SEAR design that employs a highly efficient surfactant plus mobility control measures is recommended for optimum technology performance. A summary of factors influencing SEAR cost & performance is provided in Table 2-3.

Table 2-3. Factors Influencing SEAR Cost & Performance

Factor	Influence
Permeability	• Composition of surfactant formulation • Design of surfactant flood (to maximize flooding efficiency) • Flooding duration • Labor costs
Heterogeneities	• Design of surfactant flood (to include mobility control measures) • Chemical requirement and costs • Sweep efficiency • DNAPL removal efficiency
Variations in static hydraulic gradients	• Hydraulic control (design and implementation) • Sweep efficiency • DNAPL removal efficiency

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[1] Provided as recommended minimum, actual requirement will vary from site to site.

Section 3.0: SITE/FACILITY DESCRIPTION

3.1 Demonstration Site Selection

The following criteria were used to select the demonstration site. First, a DoD site was sought as stipulated by ESTCP funding requirements. Secondly, a well-characterized site with strong indications of DNAPL contamination by a chlorinated solvent was necessary. This was due to both limited time and resources for locating DNAPL, as well as to the fact that chlorinated solvents are the most prevalent source of DNAPL contamination at DoD sites. Thirdly, a site with acceptable permeability for the practical introduction of surfactants was desired. Finally, a site with organizational and regulatory support for the proposed approach to removing DNAPL contamination was desired to expedite internal and external approval processes, as well as to provide leveraged funding.

After reviewing data from a number of sites, the first location proposed as a demonstration site was the Air Force Plant Four (AFP4), near Fort Worth, Texas. Limited site characterization was performed at this facility; however, the hydrogeology in the area of suspected DNAPL contamination was observed to be highly complex and of low permeability; furthermore, our initial efforts did not locate DNAPL. Therefore, the AFP4 site was not pursued further. Another round of data reviews and site visits was conducted, and as a result of this effort, the site that most closely fit the criteria above was the dry-cleaning facility, Site 88, at MCB Camp Lejeune, North Carolina. Details of the site and facility characteristics are provided in Section 3.2.

The MCB Camp Lejeune site provided a number of advantages. The first advantage was the strong interest voiced by the local Marine Corps and managing Navy organization (LANTDIV) for implementing the SEAR technology; this was matched by regulatory support. Since the lead organization for this project was the U.S. Navy, there was also the convenience of working with a Marine Corps facility in simplifying matters of logistical support as well as contracting. Furthermore, there were beneficial site characteristics. The DNAPL contamination at Site 88 lies in the shallow aquifer, which minimized costs for site characterization (e.g., baseline soil sampling and well installation). Also, the subsurface was relatively homogeneous; while there was an observed decrease in permeability near the base of the shallow aquifer, there were no intervening clay lenses, which simplified the test design. Finally, there was a thick aquitard underlying the shallow aquifer that served as an excellent barrier to downward DNAPL migration. While there were some aspects of the site that were not so desirable, such as the overall low permeability of the aquifer, Site 88 provided the most advantages of all the locations explored.

3.2 Demonstration Site Background

The SEAR demonstration was conducted at Site 88, the location of the Morale, Welfare, and Recreation (MWR) Dry Cleaners (Building 25) at MCB Camp Lejeune. At this site, groundwater contamination of the shallow and intermediate aquifers has resulted from the storage and usage of dry-cleaning solvents, PCE, a chlorinated hydrocarbon, and Varsol™, a petroleum distillate. PCE is still in use at this active dry-cleaning facility. The boundaries of the dissolved PCE plume in the shallow aquifer as interpreted in August 1996 are provided in Figure 1-2. Due to PCE concentrations as high as 54 mg/L in groundwater samples collected to the northwest of Building 25 (aqueous solubility of PCE at room temperature = 240 mg/L), the presence of immiscible-phase PCE (i.e., PCE DNAPL) was suspected. During site investigations conducted by the ESTCP team, local DNAPL saturations of up to 14% were detected in soil samples collected from the lower portions of the shallow aquifer, and free-

phase DNAPL was collected from several well locations. Varsol™ contamination was detected in the upper portions of the aquifer, but none as free-phase LNAPL. Gas chromatography/mass spectrometry (GC/MS) analysis of the free-phase DNAPL samples showed that they comprised primarily PCE with Varsol™ as a minor dissolved component (2-14 wt%).

3.3   Demonstration Site Characteristics

The DNAPL zone at Site 88 is located beneath Building 25, in the shallow surficial aquifer at a depth of approximately 15-20 ft (4.6-6 m), and includes an area that extends about 20 ft (6 m) north of the building. The DNAPL occurs immediately above and within a relatively low-permeability layer of silty sediments (hereafter referred to as the basal silt layer). The basal silt layer occurs from approximately 18 - 20 ft (5.5-6 m) bgs and grades finer with depth from a sandy silt to a clayey silt until reaching a thick clay layer at about 20 ft (6 m) bgs. Initial site characterization activities indicated a decreasing permeability with depth, and a permeability contrast of approximately 5:1. Additional characterization data obtained during and following the SEAR demonstration revealed that this fining downward sequence has an actual permeability contrast of approximately 10:1. Post-SEAR simulations conducted to fit the field data suggest that the DNAPL-contaminated portions of the aquifer can be roughly divided into three permeability zones: the upper zone (~15-18 ft bgs; 4.6-5.5 m bgs), the middle zone (~18-19 ft bgs; 5.5-5.8 m bgs), and the lower zone (~19-20 ft bgs; 5.8-6.1 m bgs). Additional discussion of the post-SEAR simulations is provided in Section 5.1.1. The site conceptual model, or geosystem, is shown in cross section in Figure 3-1. The approximate DNAPL boundary is shown in Figure 3-2.

The upper zone is generally characteristic of the overall shallow aquifer, which is primarily composed of fine to very fine sand and is the most permeable of the three zones. The hydraulic conductivity (K) of the upper zone is estimated to be about 5×10^{-4} cm/sec (1.4 ft/day). The hydraulic conductivity of the middle zone, which is composed predominantly of silt, is estimated to be approximately 1×10^{-4} cm/sec (0.28 ft/day), or about five times less permeable than the upper zone. The lower zone is composed predominantly of clayey silt, with a hydraulic conductivity that is believed to be approximately 5×10^{-5} cm/sec (0.14 ft/day) or perhaps even lower, although the permeability of the lower zone is not well characterized at this time. The upper- and middle-zone estimates of hydraulic conductivity are based on the analysis of pre-SEAR tracer test data from multilevel samplers (MLSs). The bottom-zone estimate of hydraulic conductivity has been supported by the results of grain-size analyses that were conducted after the completion of the SEAR demonstration, on 72 soil samples from the bottom 3 ft of the test zone. The grain-size analyses confirm that the DNAPL zone is located in a fining downward sequence, from fine sand to clayey silt, and bounded below by a clay aquitard.

A pre-SEAR PITT was conducted during May/June 1998 to measure the volume and relative distribution of DNAPL present in the test zone before surfactant flooding. The results of this pre-SEAR PITT indicated that approximately 74-88 gal (280-333 L) of DNAPL were present in the test zone (DE&S, 1999c). Average DNAPL saturations were found to be highest in the portion of the test zone that is adjacent to Building 25, at about 4.5% saturation (expressed as an average DNAPL saturation over the swept pore volume between an interwell pair of injection and extraction wells). While the pre-SEAR PITT provided valuable site characterization data, the SEAR results and the post-SEAR soil sampling results indicate that the pre-SEAR PITT underestimated the initial DNAPL volume and saturations. This is discussed further in Section 5.2, Data Assessment.

A summary of the demonstration site conditions is provided in Table 3-1.

Table 3-1. Summary of Demonstration Site Conditions at Site 88, MCB Camp Lejeune

Parameter	Value
Depth to aquitard	18-20 ft bgs (5.5 to 6.1 m bgs)
Depth to water table	7-9 ft (2.1 to 2.7 m)
Porosity of aquifer	0.3
DNAPL zone vertical thickness in aquifer	5 ft (1.5 m)
Hydraulic conductivity of the DNAPL zone[a]	1.42 ft/day (5×10^{-4} cm/sec) for the upper 3 ft of the DNAPL zone (and for the rest of the saturated zone above), 0.28 ft/day (1×10^{-4} cm/sec) for the middle 1 ft, and 0.14 ft/day (5×10^{-5} cm/sec) for the bottom 1 ft
Hydraulic conductivity of clay layer	5.76×10^{-4} ft/d (2×10^{-7} cm/sec)
DNAPL saturation	DNAPL occupies 2% of pore space on average, with a distribution of 0-4% of the pore space

(a) This is based on post-SEAR history match (i.e., data fitting) simulations.
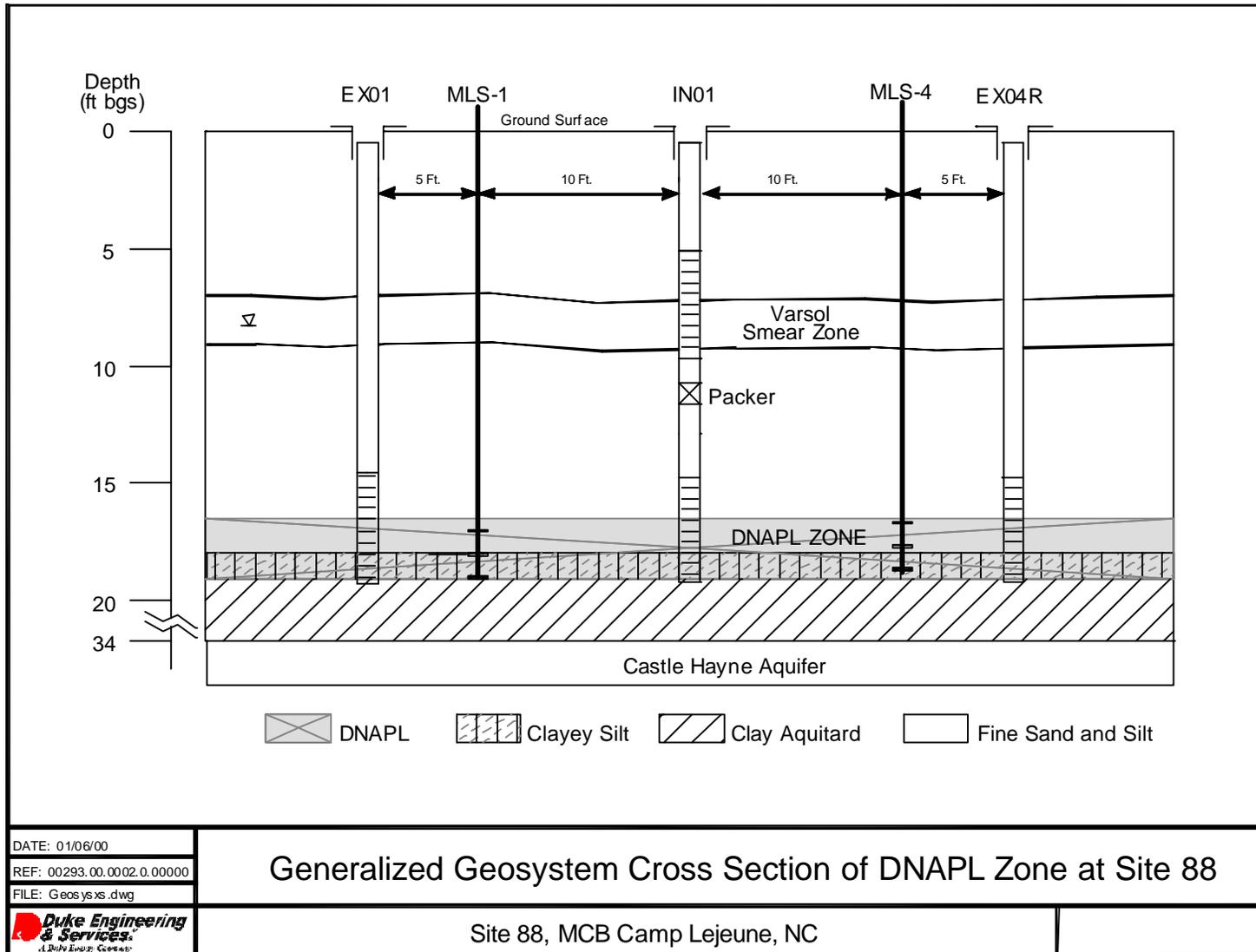
Figure 3-1. Generalized Geosystem Cross Section of DNAPL Zone at Site 88, MCB Camp Lejeune
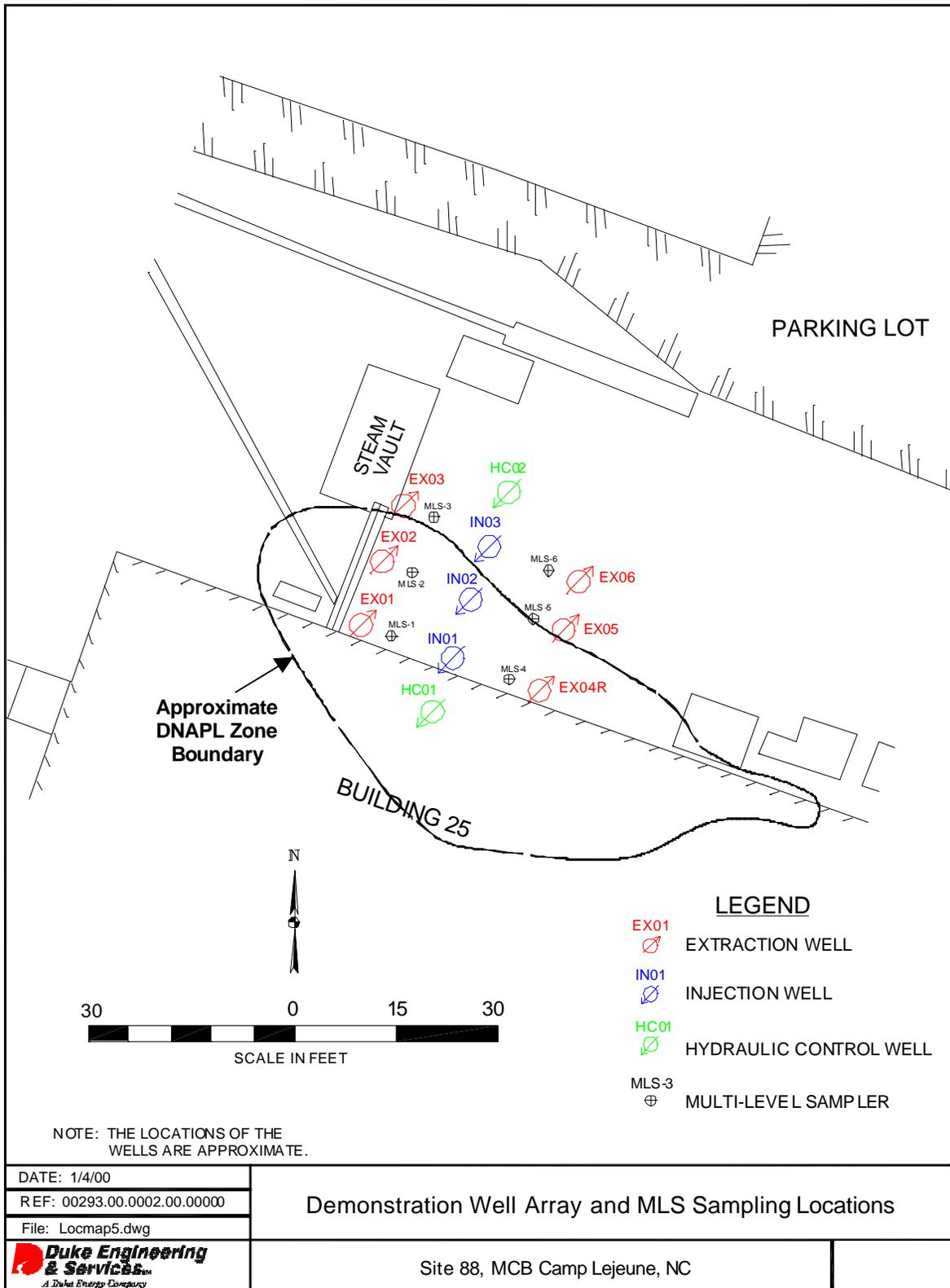
Figure 3-2. Demonstration Well Array and MLS Sampling Locations

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Section 4.0: DEMONSTRATION APPROACH

4.1   Performance Objectives

Performance objectives were set for the subsurface DNAPL remediation as well as for aboveground treatment and recovery components of the SEAR technology demonstration.

4.1.1   Subsurface DNAPL Remediation. The desired endpoint of the SEAR demonstration was to remove DNAPL down to an average residual saturation of 0.05% (an average value for DNAPL saturation throughout the swept pore volume) as determined using a post-SEAR PITT. With an estimated swept pore volume of 6,000 gallons, a final residual saturation of 0.05% corresponds to 3 gal DNAPL remaining in the test zone. With an initial estimate of 81 ± 7 gallons DNAPL in the test zone (DE&S, 1999c), this is approximately equivalent to a 96% DNAPL removal efficiency. In addition, at a minimum, 90% recovery of injected surfactant, isopropyl alcohol (IPA), and tracer was targeted. These targets were anticipated to be economically achievable at most sites where surfactants would be applied and within the resolution accuracy of the sample analytical procedures and other mathematical methods used for interpreting the final PITT and SEAR data. Discrete-depth samples collected from the MLSs during the SEAR and post-SEAR PITT were to be used in order to determine the efficiency of DNAPL removal with depth. It also was anticipated that lower-permeability contaminated zones would be locations where removal targets might not be met. Due to problems encountered in the post-SEAR PITT data analysis, soil samples collected before and after the SEAR demonstration were used to determine whether aquifer heterogeneities affected the performance of surfactant flooding and whether DNAPL contaminants had been redistributed during the surfactant flood.

4.1.2   SEAR Effluent Treatment and Surfactant Recovery. The purpose of the surfactant recovery system was to treat the extraction well effluent so that surfactant recovered from the subsurface could be reinjected into the aquifer. This treatment objective was accomplished by removing DNAPL and excess water from the extraction well effluent. The specific goal of pervaporation treatment was to remove 95% of the extracted contaminant mass, in accordance with State of North Carolina reinjection criteria. The specific goals of UF treatment were to: a) reconcentrate diluted surfactant sufficiently so that surfactant could be reinjected at 4% by weight (wt%); and b) to accomplish 90% recovery of surfactant.

4.2   Physical Setup and Operation

The SEAR demonstration at Site 88 included multiple phases of field activities from March to August 1999. Following site setup, injection/extraction operations occurred continuously for 143 days, and included a pre-SEAR water flood, surfactant flood, post-SEAR water flood, post-SEAR PITT, and post-SEAR soil sampling. A timeline showing the major tasks and their duration is illustrated in Figure 4-1. The project timeline is divided into eight phases to reflect changes in activities, flowrates, and the injected solutions (injectate). Note that surfactant flooding was extended by 10 days beyond the planned 48 days, and that postsurfactant water flooding was increased by 14 days above the original 20 days due to field observations that the subsurface system was responding more slowly to the remediation process than expected. A detailed description of the major tasks described herein can be found in Appendix G (SEAR Final Report, DE&S, 2000). Photos taken during SEAR field operations can be found in Appendix C.

March 1999

| 15 | 16 | 17 | 18 | 19 | 20 | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 | 31 |
| m | t | w | t | f | s | s | m | t | w | t | f | s | s | m | t | w |

(Cumulative Days)

0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16

SEAR Set-Up (14d)

Water Flood (8 d)

Surfactant Injection with Fresh Surfactant (37d)

April 1999

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | 21 | 22 | 23 | 24 | 25 |
| t | f | s | s | m | t | w | t | f | s | s | m | t | w | t | f | s | s | m | t | w | t | f | s | s |

17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41

April 1999

| 26 | 27 | 28 | 29 | 30 |
| m | t | w | t | f |

May 1999

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 | 31 |
| s | s | m | t | w | t | f | s | s | m | t | w | t | f | s | s | m | t | w | t | f | s | s | m | t | w | t | f | s | s | m |

June 1999

| 1 | 2 | 3 | 4 | 5 | 6 |
| t | w | t | f | s | s |

42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80 81 82 83

Surfactant Injection with Fresh Surfactant, continued (38d)

Surfactant Flood with Recycled Surfactants (10d)

Extension of the recycled surfactant flood (10 days)

Water Flood (34 days)

June 1999

| 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 |
| m | t | w | t | f | s | s | m | t | w | t | f | s | s | m | t | w | t | f | s | s | m | t | w |

July 1999

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 |
| t | f | s | s | m | t | w | t | f | s | s | m | t | w | t | f | s | s | m |

84 85 86 87 88 89 90 91 92 93 94 95 96 97 98 99 100 101 102 103 104 105 106 107 108 109 110 111 112 113 114 115 116 117 118 119 120 121 122 123 124 125 126

Water Flood continued (34 days)

Tracer Injection (6 days)

Water Flood (34 days)

July 1999

| 20 | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 | 31 |
| t | w | t | f | s | s | m | t | w | t | f | s |

August 1999

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 | 31 |
| s | m | t | w | t | f | s | s | m | t | w | t | f | s | s | m | t | w | t | f | s | s | m | t | w | t | f | s | s | m | t |

127 128 129 130 131 132 133 134 135 136 137 138 139 140 141 142 143 144 145 146 147 148 149 150 151 152 153 154 155 156 157 158 159 160 161 162 163 164 165 166 167 168 169

Water Flood continued (34 days)

PITT completed on 8/16 and water flooding continued until 8/19 during soil sampling

System Teardown and Post-Demo sampling (13 days)

PA soil sampling (3 days)

GW sampling for Varsol (2 days)

Figure 4-1. Project Timeline for SEAR Demonstration and PITT at Site 88, MCB Camp Lejeune

Site setup included preparation of the following subsurface DNAPL remediation system components: the well field (described below); the tank farm, consisting of three 3,000-gallon tanks and two 1,650-gallon tanks, pumps and containment liner; and the Control Trailer, which housed the Supervisory Control and Data Acquisition (SCADA) system and Autocollector (i.e., the automatic sample collector). In addition, setup included testing and calibration of the following SEAR effluent treatment systems: the pervaporation system and the ultrafiltration unit. The pervaporation and ultrafiltration systems, including appurtenant equipment, such as feed and holding tanks and analytical equipment, were housed in a large field tent that was situated east of the well field and the control trailer. The full SEAR equipment layout, including the subsurface remediation and effluent treatment systems, is provided in Figure 4-2. The arrangement of equipment inside the field tent is shown on Figure 4-3. Photos of various system components can be found in Appendix C.

Installation of the SEAR demonstration well field was not a part of the SEAR operations, since it had been completed much earlier for conducting free-phase DNAPL removal and for the pre-SEAR conservative and partitioning interwell tracer tests. The well field is situated in the portion of the DNAPL zone that lies just outside and north of Building 25. It consists of a total of three injection and six extraction wells arranged in a $3 \times 3 \times 3$ divergent line-drive configuration (injected fluids are forced towards oppositely located extraction wells with injection/extraction well pairs arranged in parallel lines). In addition, hydraulic control wells are located at each end of the centrally located row of injection wells. Thus, the test-zone well field comprises 11 wells in total. The test area footprint formed by the $3 \times 3 \times 3$ array of injection and extraction wells is 20 ft wide by 30 ft long. The well field and geosystem is shown in cross section in Figure 3-1. Multilevel samplers were installed at six locations, three in December 1997 and three more in December 1998, to monitor discrete depths in the test zone. Each MLS location consisted of a bundle of three sampling points to allow sampling from three discrete depths. One MLS bundle was installed between each injection-extraction well pair, as shown in Figures 3-1 and 3-2. The multilevel sampling points at MLS-1, MLS-4, MLS-5, and MLS-6 were installed at discrete depths of approximately 16.5, 17.5, and 18.5 ft bgs, while the points at MLS-2 and MLS-3 were installed at depths of 17.0, 18.5, and 19.5 ft bgs.

The surfactant formulation was designed specifically for this demonstration to meet two objectives: (1) to maximize DNAPL solubilization, and (2) to maximize surfactant recovery by the UF system. Extensive laboratory testing was conducted to optimize these dual objectives. The result was the selection of a custom surfactant, Alfoterra 145-4-PO sulfate™, that was manufactured by Condea Vista Company for the SEAR demonstration. The surfactant injectate formulation consisted of 4 wt% Alfoterra 145-4PO sulfate™ surfactant, 16 wt% IPA, and 0.16-0.19 wt% calcium chloride ($CaCl_2$) mixed with source water (i.e., site potable water). Although originally both sodium chloride and calcium chloride were used as electrolytes in the surfactant formulation, soil column testing showed that the sole use of calcium chloride was necessary to prevent the mobilization of soil fines in the Camp Lejeune soils.

Due to the low permeability of the DNAPL-contaminated sediments at Site 88, as well as the shallow conditions, injection and extraction flowrates during the SEAR demonstration were low relative to flowrates used at other surfactant flooding projects. The total rate of surfactant injection (i.e., combined rate for all three injection wells) was 0.4 gpm (1.5 L/min) and the total extraction rate (i.e., combined rate for all six extraction wells) was 1 gpm (3.8 L/min). Flowrates were varied during different phases of operations to improve the sweep of surfactant solution through the more highly contaminated sections of the test zone (i.e., near the building). In general, flowrates were increased in the well trio adjacent to the building (EX01, IN01, EX04R) and decreased in the well trio farthest from the building (EX03, IN03, EX06). Flowrates during the surfactant flood and post-SEAR water flood and PITT are shown in Table 4-1.
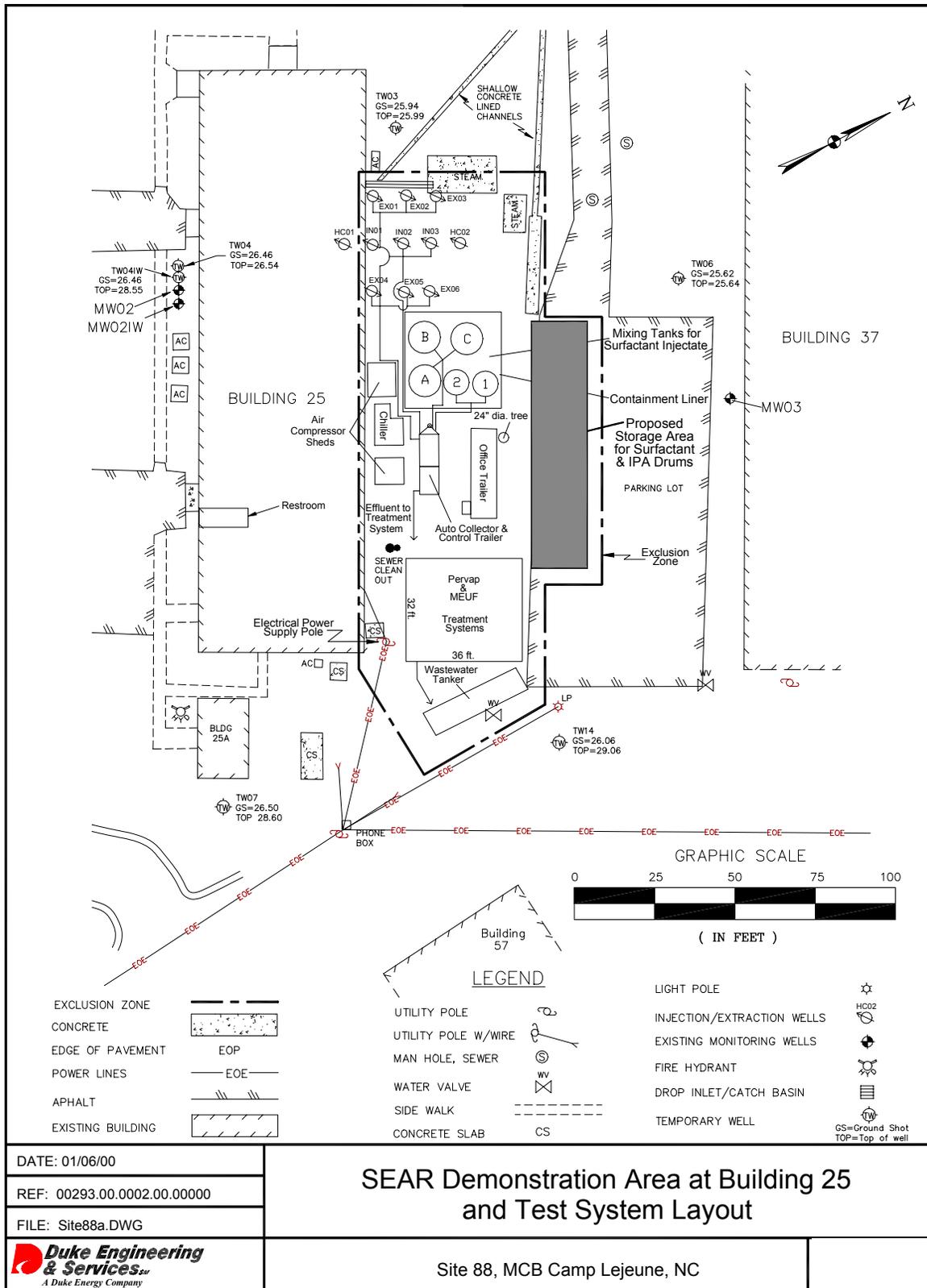
Figure 4-2. SEAR Demonstration Area at Building 25 and Test System Layout
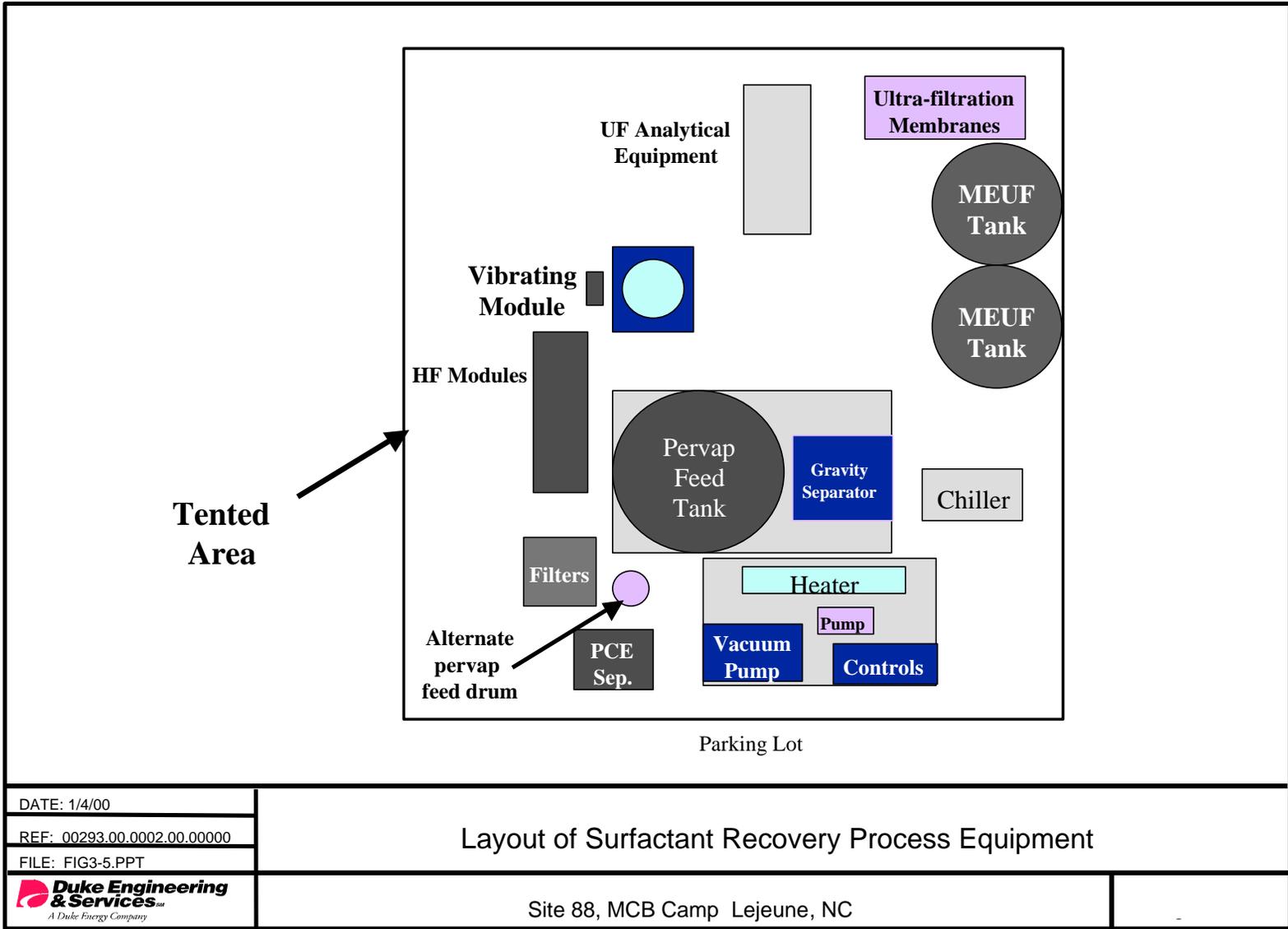
Figure 4-3. Layout of Surfactant Recovery Process Equipment

Table 4-1. Flowrates During the Surfactant Flood and Post-SEAR Water Flood and PITT

Well ID	Surfactant Flood Phase I (27 days) *Design Rates* (gpm)	Surfactant Flood Phase II (31 days) *Revised Rates* (gpm)	Post-SEAR Water Flood Phase I (25 days) *Revised Rates* (gpm)	Post-SEAR Water Flood Phase II (9 days) *Design Rates* (gpm)	Post-SEAR PITT (40 days) *Design Rates* (gpm)
IN01	0.13	0.17	0.25	0.20	0.20
IN02	0.13	0.13	0.20	0.20	0.20
IN03	0.13	0.10	0.15	0.20	0.20
IN01U	0.08	0.08	0.08	0.08	0.08
IN02U	0.08	0.08	0.08	0.08	0.08
IN03U	0.08	0.08	0.08	0.08	0.08
EX01	0.17	0.22	0.33	0.25	0.25
EX02	0.17	0.17	0.25	0.25	0.25
EX03	0.19	0.14	0.21	0.28	0.28
EX04	0.17	0.22	0.33	0.25	0.25
EX05	0.17	0.17	0.25	0.25	0.25
EX06	0.17	0.13	0.19	0.25	0.25
HC01	0.20	0.20	0.30	0.30	0.30
HC02	0.20	0.20	0.30	0.30	0.30

ID = identification.

During the 58-day surfactant flood, 29,700 gal (112,000 L) of the surfactant mixture was injected, which is equivalent to approximately five test-zone pore volumes, with a residence time of about 12 days per pore volume. The total mass injected was 9,718 lb (4,410 kg) surfactant, 38,637 lb (16,620 kg) IPA, and 427 lb (194 kg) $CaCl_2$. This includes 1,806 lb (820 kg) of recovered surfactant that was reinjected during the latter 20 days of surfactant flooding. During the surfactant flood, lateral hydraulic control was accomplished by injecting source water with 0.16-0.19 wt% $CaCl_2$ in solution into the two hydraulic control wells, HC01 and HC02. Vertical hydraulic control above the test zone was implemented by injection of the source water and $CaCl_2$ solution into the upper screens of the injection wells while surfactant was being simultaneously injected into the lower screens of the injection wells, IN01, IN02, and IN03. The two different injectates were separated from each other by an inflatable packer located between the upper and lower screens in the three injection wells. The clay layer beneath the DNAPL zone provided hydraulic containment below the test zone. The total surfactant injection rate was 0.4 gpm, initially split evenly between the three injection wells (0.133 gpm/well) as called for in the SEAR design. The total extraction rate (i.e., cumulative flowrate for the six extraction wells) during the surfactant flood was 1.0 gpm. Flowrates at individual wells were varied during different phases of the demonstration, as discussed earlier; however, the total flowrates were unchanged. The 58-day surfactant flood was followed, without interruption, by 74 days of water flooding, the last 40 days of which included the post-SEAR PITT.

Injection rates were controlled by manual needle valves in the control trailer and monitored by the SCADA system. Pneumatic submersible pumps were utilized for extraction. Extraction rates were controlled via pneumatic controllers located at each extraction wellhead, and were monitored by the SCADA system.

Free-phase DNAPL recovery during surfactant flooding and post-surfactant water flooding operations was conducted every 2-3 days using a peristaltic pump to remove DNAPL that slowly accumulated in the sumps of several wells. The volume of free-phase DNAPL recovered was recorded for each well.

The aboveground treatment processes were operated for more than two months on a continuous basis to treat the SEAR effluent to enable surfactant recovery for reuse. Wastewater generated from the aboveground treatment processes was sent to a wastewater tanker located to the east of the field tent (see Figure 4-2). A total of three recycled surfactant batches were mixed and injected between May 13 and June 3, 1999. Although the surfactant recovery processes continued to operate for a short duration beyond this period, no additional surfactant recovered was reinjected. Following this period, SEAR effluent was delivered to the wastewater tanker for treatment at an air stripping facility located on base.

4.3 Sampling & Monitoring Procedures

SEAR monitoring included regular collection of samples for analysis in accordance with the sampling and analysis plan (DE&S, 1999a). System operations also were continually monitored according to the SEAR work plan (DE&S, 1999b).

The surfactant flood required a variety of sample collection activities from numerous locations including:

- Injectate tank batches before and during injection
- Extracted fluids from each of six extraction wells (EX01 to EX06)
- Groundwater from three MLS locations
- Groundwater sampling from monitoring wells located both inside and outside the test zone
- Influent and effluent at the aboveground treatment systems
- Post-SEAR soil core sampling.

Sampling activities are summarized below. The sampling locations, monitoring objectives, analytes, and sampling frequencies are summarized in Table 4-2. Following Table 4-2 is a brief description of each sampling activity. For more detailed sampling, analysis, and shipping procedures see the Sampling and Analysis Plan (DE&S, 1999a).

Samples were collected from the top and bottom of the batch mixing tanks for analysis to verify that each injectate batch was well mixed and met design specifications prior to injection. Surfactant batch samples were analyzed at off-site laboratories for surfactant, IPA, and calcium. In addition, phase behavior testing was conducted on site on samples from each surfactant batch mixture. The onsite phase behavior testing was done in order to provide field confirmation, prior to injection of the batch, that each surfactant batch behaved as a Winsor Type I or Type III system. Tank batches used strictly for hydraulic control and water flooding contained only $CaCl_2$ as a chemical additive, and were qualitatively analyzed on site for electrolyte concentrations by measuring specific conductance.

Groundwater samples were collected from all extraction wells (EX01-EX06) and from selected MLSs (MLS-1, MLS-4, and MLS-2) throughout the demonstration to monitor the recovery of both PCE and injectate chemicals from the treatment zone. Because of the fine-grained sediments in the test zone, not all of the selected MLS sampling points produced sufficient sample volumes for analysis.

Table 4-2. Summary of Sampling Activities During the SEAR Demonstration

Sampling/Monitoring Location	Monitoring Objective	Analytes or Measurements	Sampling Frequency
Fresh Surfactant Tank Batches	Evaluate injectate batches per design specifications	Surfactant, IPA, Ca^{2+}	One sample from top and bottom of each tank batch
Hydraulic Control and Water Flood Tank Batches	Evaluate approximate electrolyte concentration	Ca^{2+}	One sample from top and bottom of each tank batch
Extraction wells: EX01 to EX06	SEAR performance	PCE, surfactant, IPA	Every 4 days
MLS-1, MLS-2, and MLS-4	SEAR performance	PCE, surfactant, IPA	Every 4 days
MW02, MW02IW, RW03, RW04, RW06	Evaluate hydraulic control laterally outside the treatment zone	Surfactant, IPA	Monthly
MW02, MW03, MW05	Evaluate hydraulic control laterally outside the treatment zone	Arsenic[a]	Monthly
WP01AQT, WP02AQT, MW10IW	Evaluate hydraulic control directly beneath the treatment zone	Surfactant, IPA, Arsenic	Monthly
Pervaporation system: influent and effluent	Evaluate contaminant and IPA removal efficiency from SEAR fluids	PCE, Varsol™ marker compounds, IPA	PCE, IPA: three samples per week Varsol™ and PCE (by GC/MS): One sample per week
MEUF system: influent and effluent; also Pervaporation effluent	Evaluate surfactant recovery efficiency from SEAR fluids	Surfactant	One sample per day
Recovered surfactant	Determine concentration of injectate chemicals before reconstituting mixture for reinjection	Surfactant, Ca^{2+}, PCE	One sample from top and bottom of each tank batch

Table 4-2. Summary of Sampling Activities During the SEAR Demonstration (Continued)

Sampling/Monitoring Location	Monitoring Objective	Analytes or Measurements	Sampling Frequency
Remixed surfactant injectate for reinjection	Evaluate concentration of injectate chemicals and contaminants before reinjection	Surfactant, IPA, Ca^{2+}, PCE, Varsol™ marker compounds	One sample from top and bottom of each tank batch
Post-SEAR soil cores	Evaluate the performance of the surfactant flood to remove in situ DNAPL from the treatment zone	VOCs	One sampling event at the conclusion of the demonstration: 60 samples collected with methanol preservation from 12 soil boring locations within the treatment zone, with continuous core sampling from the bottom 3 feet of the shallow aquifer
Injection and extraction flow meters	To monitor and maintain specified flowrates	Flowrates	Continuous electronic monitoring and daily manual checks
Water levels: at wells located inside the treatment zone	To monitor and evaluate the status of hydraulic control	Water levels	Continuous electronic monitoring and daily manual checks
Water levels: at wells located outside the treatment zone	To monitor and evaluate the status of hydraulic control	Water levels	Weekly manual monitoring

(a) Arsenic was present in the injectate as a minor impurity in the dry bulk $CaCl_2$

The MLS sampling points that were monitored regularly include: MLS-1T, MLS-1B, MLS-2T, MLS-2M, MLS-4T, and MLS-4B (where T = top, M = middle, and B = bottom monitoring point). The locations of the SEAR wells and MLSs are shown in Figures 3-2 and 4-4. A sampling frequency of every 4 days throughout the SEAR demonstration was chosen as a moderate level sampling frequency which provided sufficient data yet minimized analytical costs for the demonstration.

Hydraulic control monitoring was also conducted during the demonstration by sampling wells located both outside as well as beneath the treatment zone to evaluate the effectiveness of hydraulic control measures to prevent injectate migration outside of the treatment zone. Hydraulic control monitoring was conducted on a monthly basis. Wells monitored for lateral hydraulic control evaluation were: MW02, MW02IW, MW03, MW05, RW03, RW04, and RW06. In addition, three wells were sampled to monitor directly beneath the treatment zone for downward hydraulic control: aquitard monitoring points WP01AQT and WP02AQT (sampling points located approximately 6 ft and 6 ft,

N

BUILDING 27

MW05

MW03

PARKING LOT

SHALLOW
CONCRETE
LINED
CHANNELS

STEAM
VAULT

HC02

EX03
MLS-3
EX02   MW10IW   IN03
MLS-2   WP02AQT   MLS-6   EX06
RW01   WP01AQT   IN02
AC   MLS-5
MLS-1   EX05
EX01   RW02   IW01
IN01
MLS-4
EX04R
RW03   HC01   EX04   RW04
Air
Compressor
Shed   Chiller   Air
RW06   Compressor
Shed

BUILDING 25

Former Waste PCE
Disposal Point

MW02IW
MW02

AC   AC
AC

Legend

HC01
      - Hydraulic Control Well

MW02   RW01
      - Monitor Well   - Recovery Well

EX02   IN01
      - Extraction Well   - Injection Well

0   25   50

Scale in Feet

| DATE: 4/24/00	DNAPL Source-Zone Investigations:
REF: 00293.00.0002.00.00000	Locations of Soil Borings, CPT Pushes, and Wells
FILE: New_base.dwg	
	Site 88, MCB Camp Lejeune, NC

Figure 4-4. SEAR Wellfield and Monitoring Locations, Site 88, MCB Camp Lejeune

respectively, below the top of the clay layer), and well MW10IW in the upper Castle Hayne Aquifer (screened just below the bottom of the clay aquitard). Hydraulic control monitoring locations are shown in Figure 4-4. Monthly monitoring was considered to be a sufficient sampling frequency for hydraulic control parameters since changes in water quality due to loss of hydraulic control were expected to occur slowly at the monitoring locations. Hydraulic control analytes included surfactant, IPA, and arsenic (a minor impurity in the dry bulk $CaCl_2$). PCE was also monitored at these wells although not strictly as a hydraulic control analyte since dissolved PCE was already present at most monitoring locations prior to the surfactant flood.

As surfactant and PCE were recovered at the extraction wells during the SEAR demonstration, the well field effluent was directed to the aboveground treatment systems in order to remove DNAPL contaminant and to recover the surfactant. The separation of DNAPL, in the form of solubilized volatile organic compounds (VOCs), from the surfactant/groundwater mixture was accomplished using pervaporation. To assess pervaporation performance, samples were collected at the influent to the pervaporation system, and from the residual stream of each of the two pervaporation units. These samples were analyzed for PCE as well as for components of the secondary contaminant at the site, Varsol™, to determine the efficiency of contaminant removal. The pervaporation effluent was then directed to the MEUF for surfactant recovery. To evaluate MEUF effectiveness, samples collected from the feed, permeate, and retentate streams were analyzed for surfactant in order to perform a surfactant mass balance. Neither the pervaporation nor the MEUF systems were designed to recover IPA. Effective IPA removal by a nonporous membrane process (i.e., pervaporation) would have required a thicker and more hydrophilic membrane that would not have been appropriate for PCE removal. Likewise, IPA recovery by a porous membrane process (i.e., membrane filtration) would have required a much lower molecular weight cutoff membrane that would not have been cost-effective for recovering surfactant micelles.

Once sufficient volume of surfactant was recovered by the MEUF system, the recovered batch was transferred to an injectate mixing tank for reinjection. Because the recovery process could not preserve the original design concentrations of the surfactant injectate (i.e., surfactant, IPA, and calcium concentrations), the recovered batch had to be reconstituted. This required a multistep process: (1) sampling and analysis of the recovered surfactant batch; (2) reconstitution of the batch concentrations to SEAR design injectate specification; and (3) filtration to remove iron-organoflocculent (a byproduct of SEAR application in the Site 88 sediments and followed by surfactant recovery) prior to reinjection. Reconstitution of the recovered surfactant to design injectate concentrations required the addition of fresh, unused surfactant (to dilute the resulting super concentration of calcium by MEUF), and additional IPA and source water. Once reconstituted, the recovered surfactant batch was sampled and analyzed before reinjection under the same protocol followed for all other surfactant batches to ensure that each batch met design specifications, as discussed previously in this section.

In addition to the many sampling activities during the SEAR demonstration, system operations were also continually monitored according to the SEAR Work Plan (DE&S, 1999b). Injection and extraction flowrates were monitored continuously by the SCADA system, and flowrates were adjusted as necessary to maintain flow at design specifications. Manual flowrate measurements were conducted daily to verify that the electronic flowmeters were accurate. Electronic flowmeters were adjusted or recalibrated if found to be in error of greater than 10% per the SEAR Work Plan (DE&S, 1999b). With the use of electronic pressure transducers, water levels in all injection and extraction wells were monitored continuously by the SCADA system. Water levels also were measured manually on a daily basis to verify that the electronic water-level measurements were accurate, and pressure transducers were adjusted or recalibrated to match actual water levels when electronic measurements deviated from

manual measurements by greater than 0.2 feet. In addition, water levels were measured manually at monitoring wells located outside the treatment zone on a weekly basis. Water level data was used to evaluate the status of hydraulic control.

At the conclusion of the SEAR demonstration, soil core samples were collected from the treatment zone for performance assessment of the surfactant flood. The soil core samples were preserved in the field with methanol to minimize contaminant losses by volatilization from the soil samples.

4.4   Analytical Procedures

The analytical methods used to monitor and assess SEAR performance are summarized in Table 4-3. Standard quality assurance (QA) protocol was followed for all analyses, such as conducting analysis of duplicates, calibration check standards, and method blanks at a minimum frequency of 5% for all samples analyzed. Further details of the analytical methods, the QA protocol, and the laboratories that conducted the analyses can be found in the Sampling and Analysis Plan (DE&S, 1999a).

Table 4-3. Analytical Methods

Analyte	Analytical Method	
	Subsurface	Surface
Surfactant	Hyamine titration	Liquid chromatography
IPA, PCE[a]	EPA 8015 modified	EPA 8015 modified
PCE[b]	EPA 8260	EPA 8260
Varsol[c]	EPA 8260	EPA 8260
Calcium	EPA 200.7	–
Arsenic	EPA 206.2	–
Alcohol Tracers[d]	EPA 8015 modified	–
VOCs [e]	EPA 8260	–

(a) SEAR samples for high PCE concentrations in the test zone and PCE samples from the pervaporation system that were analyzed on site.

(b) Monitoring samples for low PCE concentrations outside the test zone and other PCE samples (pervaporation) sent for off-site analysis.

(c) Varsol™ marker compounds: decane, undecane and 1,3,5-trimethylbenzene.

(d) Alcohol tracers: 1-propanol, *sec*-butanol, 1-hexanol, 1-heptanol, and 2-ethyl-1-hexanol.

(e) Post-SEAR soil core samples collected from within the treatment zone and analyzed for performance assessment of the surfactant flood.

Section 5.0: PERFORMANCE ASSESSMENT

5.1   Performance Data

         This section provides a summary of the significant results from surfactant flooding and recovery operations. For more complete details of the SEAR demonstration results, see Section 7 of the SEAR Final Report (DE&S, 2000) in Appendix G.

5.1.1   Subsurface DNAPL Remediation. A significant increase in the extraction well effluent PCE concentration was observed in several extraction wells due to surfactant flooding. At extraction well EX01, the effluent PCE concentration increased from an average of approximately 200 mg/L to about 2,800 mg/L at the peak breakthrough. At EX04R, the PCE concentration increased from 80 mg/L to approximately 1,000 mg/L at the peak. In addition to the extraction wells, PCE concentrations were also measured in MLS points located next to EX01 and EX04R. At all MLS locations, there were three sampling depths near the base of the shallow aquifer referred to as the top, middle and bottom sampling points, respectively. However, not all of these sampling points yielded samples that could be accurately analyzed. For example at MLS-1T, due to a vacuum leak in the sampling system, samples were not analyzed for PCE. The leak was corrected for the post-SEAR PITT, and the effluent PCE concentrations measured at that time showed that PCE concentrations were essentially nondetectable. The PCE concentration history for MLS-4T is shown in Figure 5-1. Much higher peak PCE concentrations were observed at MLS-4T than at nearby extraction well EX04R, as expected from the placement of the MLS inside the test zone, which prevented dilution of samples by groundwater from outside the test zone. At MLS-4T, the PCE concentration at the start of the surfactant flood was 5 mg/L. The effluent PCE concentration was seen to increase rapidly to 10,860 mg/L before declining to nondetectable concentrations at the end of the post-SEAR PITT. This is an excellent indication that the surfactant was highly effective in solubilizing and remediating DNAPL in the upper zone in the vicinity of MLS-4T. It should be recalled that the SEAR demonstration was 143 days including the post-SEAR PITT. Although the post-SEAR PITT required 40 days of flooding activities, had it not been conducted, the total duration of the SEAR demonstration (not inclusive of any pre-SEAR site preparation and characterization activities such as flooding to remove mobile DNAPL or tracer tests) would have required approximately 127 days, based on the actual recoveries of injected chemicals. The original planned duration of the SEAR demonstration was 119 days; however, it was extended for a period of 10 days for additional surfactant flooding by recycled surfactant as well as for an additional 14 days of water flooding to bring down surfactant concentrations prior to injecting tracers for the post-SEAR PITT without interference.

         Sample collection was unsuccessful from the midlevel sampling points MLS-1M and MLS-4M during the surfactant flood. These MLS locations did not produce enough sample volume for analysis, even after pumping with a peristaltic pump for up to 30-45 minutes. However, a few samples were successfully collected from MLS-4M at the end of the post-SEAR water flooding and the final PCE concentration in these samples was nondetectable. Samples collected from bottom level at MLS-1B and MLS-4B were entirely composed of free-phase DNAPL at the beginning of the surfactant flood. Samples from MLS-4B continued to produce large fractions of free-phase DNAPL with just a small fraction of the aqueous phase until the end of the post-SEAR PITT, and therefore, few PCE concentration results are available for this point. The samples from MLS-1B, however, stopped producing large fractions of free-phase DNAPL after 25 days of surfactant flooding, though small droplets of DNAPL were observed in a number of subsequent samples. The PCE concentration history of MLS-1B is shown in Figure 5-2. From this figure, it can be seen that a maximum PCE concentration of approximately 23,000 mg/L was
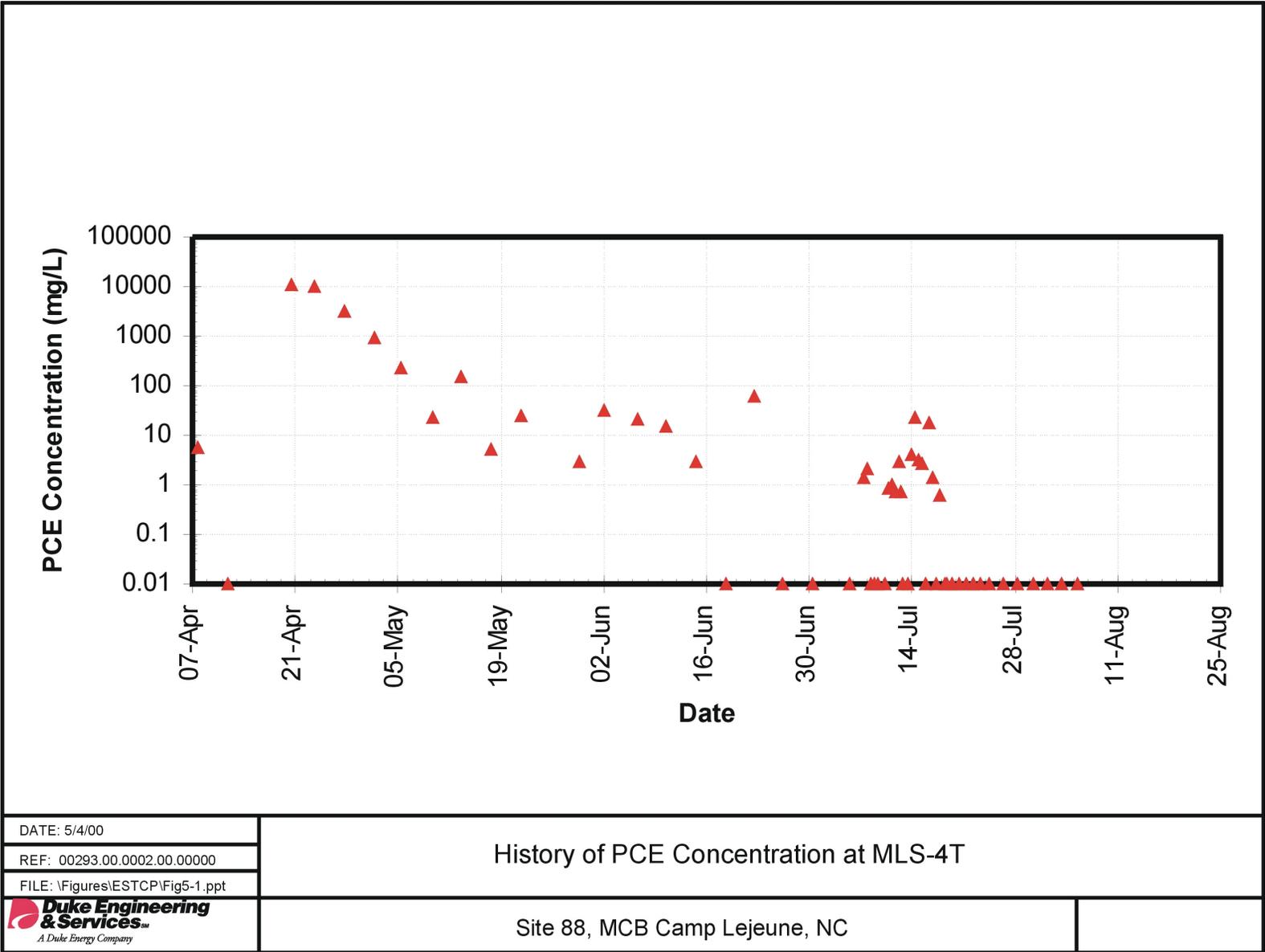
Figure 5-1. History of PCE Concentrations at MLS-4T

Figure 5-2. History of PCE Concentrations at MLS-1B

observed, followed by a decline to 180 mg/L at the end of the post-SEAR PITT. The presence of relatively high aqueous PCE concentrations at the end of the demonstration suggests that some DNAPL still remains in the zone adjacent to MLS-1B.

A gradient in DNAPL contamination with distance from the building can be inferred by examining the PCE concentration curves for EX01, EX02, and EX03 in Figure 5-3 and the PCE concentration curves for EX04R, EX05, and EX06 in Figure 5-4. That the decreasing PCE concentrations are not a mere anomaly of a lateral heterogeneity in permeability difference can be seen by studying the pre-SEAR soil sampling and conservative interwell tracer test (CITT) and PITT data. (For these results, the reader is referred to the DNAPL Site Characterization Report, DE&S, 1999c.) PCE concentration data obtained from the top and middle sampling points MLS-2T and MLS-2M (located at 17.0 and 18.5 ft bgs, respectively) during the surfactant flood are shown in Figures 5-5 and 5-6. The data from MLS-2T indicates that PCE concentrations rapidly declined to below detectable concentrations by the end of the demonstration. The data from MLS-2M indicates that PCE concentrations in the middle portion of the basal silt increased to approximately 1,000-2,000 mg/L as a result of surfactant flooding. PCE concentrations at MLS-2M later decreased by the end of the demonstration; however, PCE removal at this location was incomplete.

At EX-03 and EX-06, the extraction wells farthest from the building, PCE concentrations remained low, not exceeding 20 mg/L throughout the entire SEAR demonstration, most likely indicating that there was little DNAPL in the vicinity of these locations. However, at all extraction wells, the observed peak concentrations of surfactant-enhanced PCE solubilization were lower by approximately an order of magnitude than predicted from the final design simulations. This can be understood by comparing the final design simulation, ISA26m, to an earlier design simulation, ISA7m.

Figure 5-7 compares the PCE concentrations at EX01 to those predicted by ISA26m and ISA7m. ISA7m predicted a broad peak, with a maximum concentration of 1,500 mg/L, which is very similar to the observed PCE concentrations at EX01, whereas ISA26m predicted a sharp peak with maximum concentration of 25,000 mg/L. Simulation ISA7m clearly provides a superior match to observed PCE concentrations compared to ISA26m. The primary differences in the model between ISA7m and ISA26m lie in the permeability values assigned to gridblocks for the bottom 2 feet of the model and in the injection and extraction flowrates used. ISA26m predicted effluent surfactant and IPA concentrations in most of the extraction wells, which agreed reasonably well with the field data, taking into account the modifications in the flowrates as well as the duration of surfactant injection. Therefore, it is assumed that the difference between the flowrates used in the ISA7m and ISA26m model runs did not have a significant impact on the predicted PCE effluent concentrations. Also, the proportion of extraction to injection flowrates used for ISA7m and ISA26m are the same. A comparison of the effluent surfactant and IPA concentrations at EX01 to the ISA26m predicted values is given in Figures 5-8 and 5-9, respectively. In ISA7m, the permeability of the bottom 2 ft was set at 80 millidarcies (md), which is five times lower than the permeability set for the upper portions of the aquifer (i.e., 400 md), whereas for ISA26m, only the bottom 1 foot was assigned a reduced permeability at (a higher value of) 100 md while the remaining portions of the aquifer were kept at 400 md. That ISA7m provided the superior match indicates that the aquifer conditions assumed for ISA7m are more representative of the actual aquifer conditions. Therefore, it can be inferred that the permeability contrast between the less-permeable basal silt layer and the overlying fine sand is at least a factor of 5, and the low-permeability basal silt layer is probably greater than 1 ft in thickness. Under these conditions, much of the surfactant will bypass the bottom zone and flow through the more permeable upper zone. This "layering" phenomenon will therefore cause partial remediation of the lower permeability bottom zone as was observed during the field demonstration.
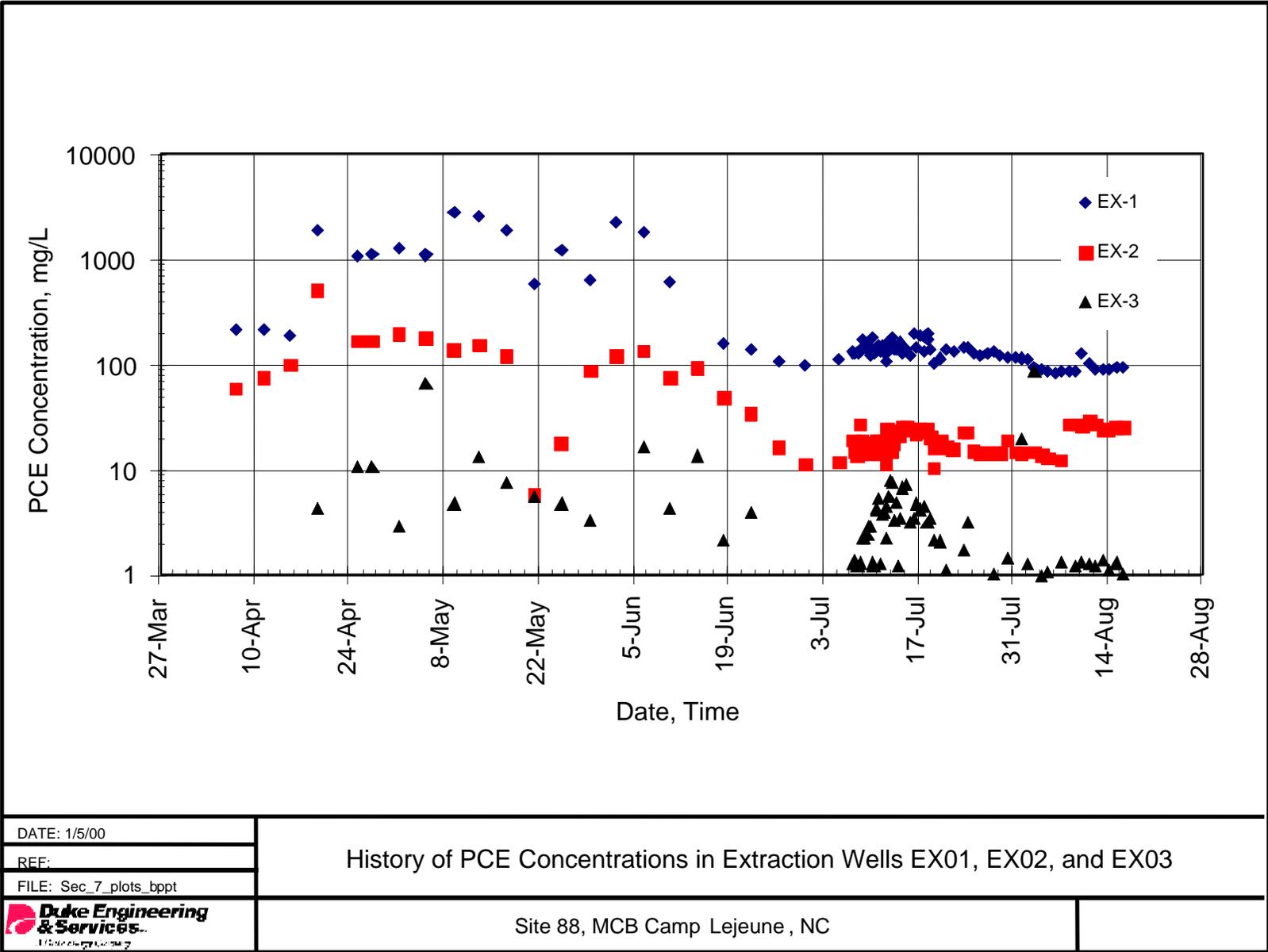
Figure 5-3. History of PCE Concentrations in Extraction Wells EX01, EX02, and EX03

DATE: 1/5/00	
REF: 00293.00.0002.00.00000	History of PCE Concentrations in Extraction Wells EX04, EX05, and EX06
FILE: PCE Data.ppt	
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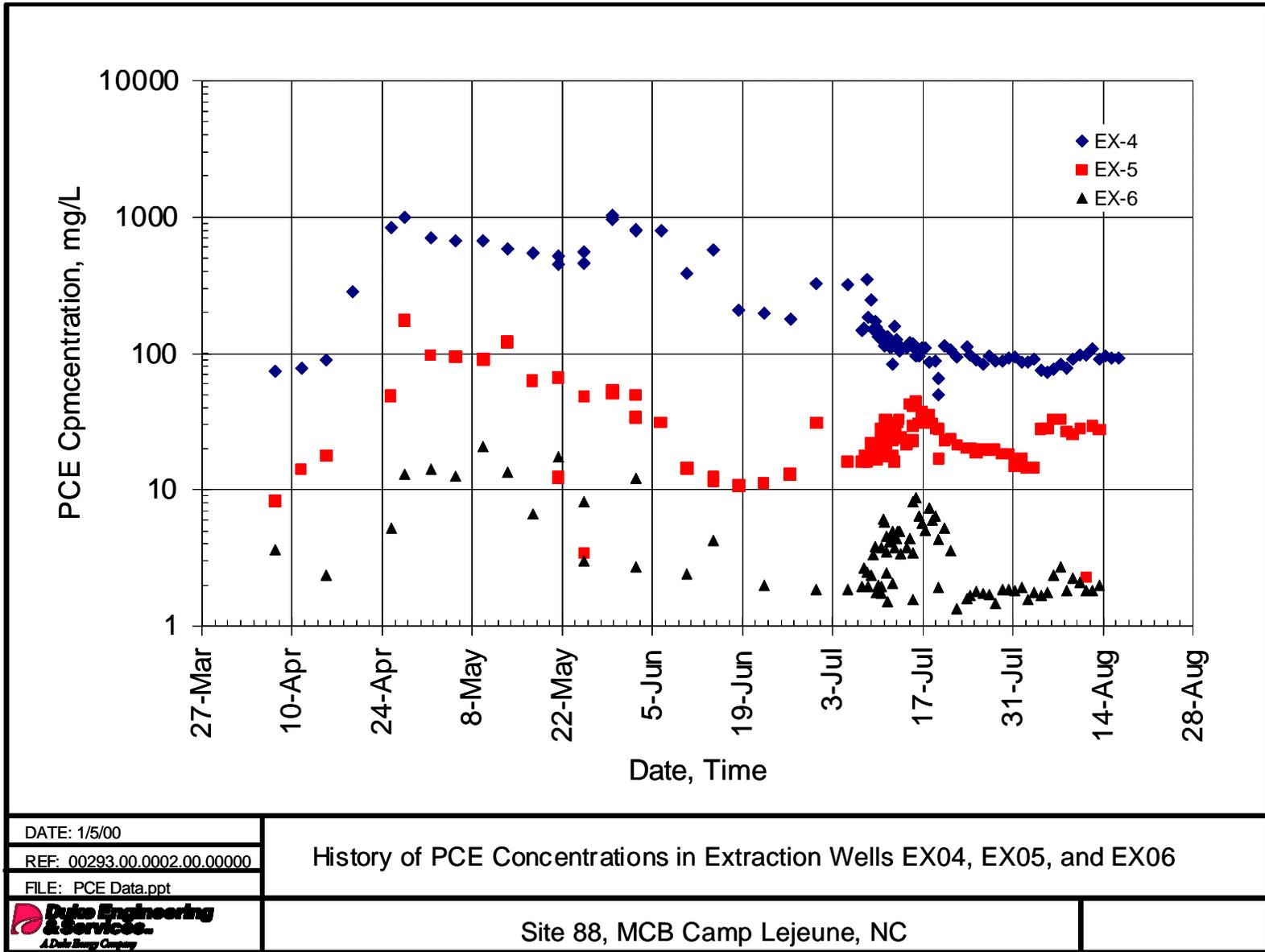
Figure 5-4. History of PCE Concentrations in Extraction Wells EX04R, EX05, and EX06
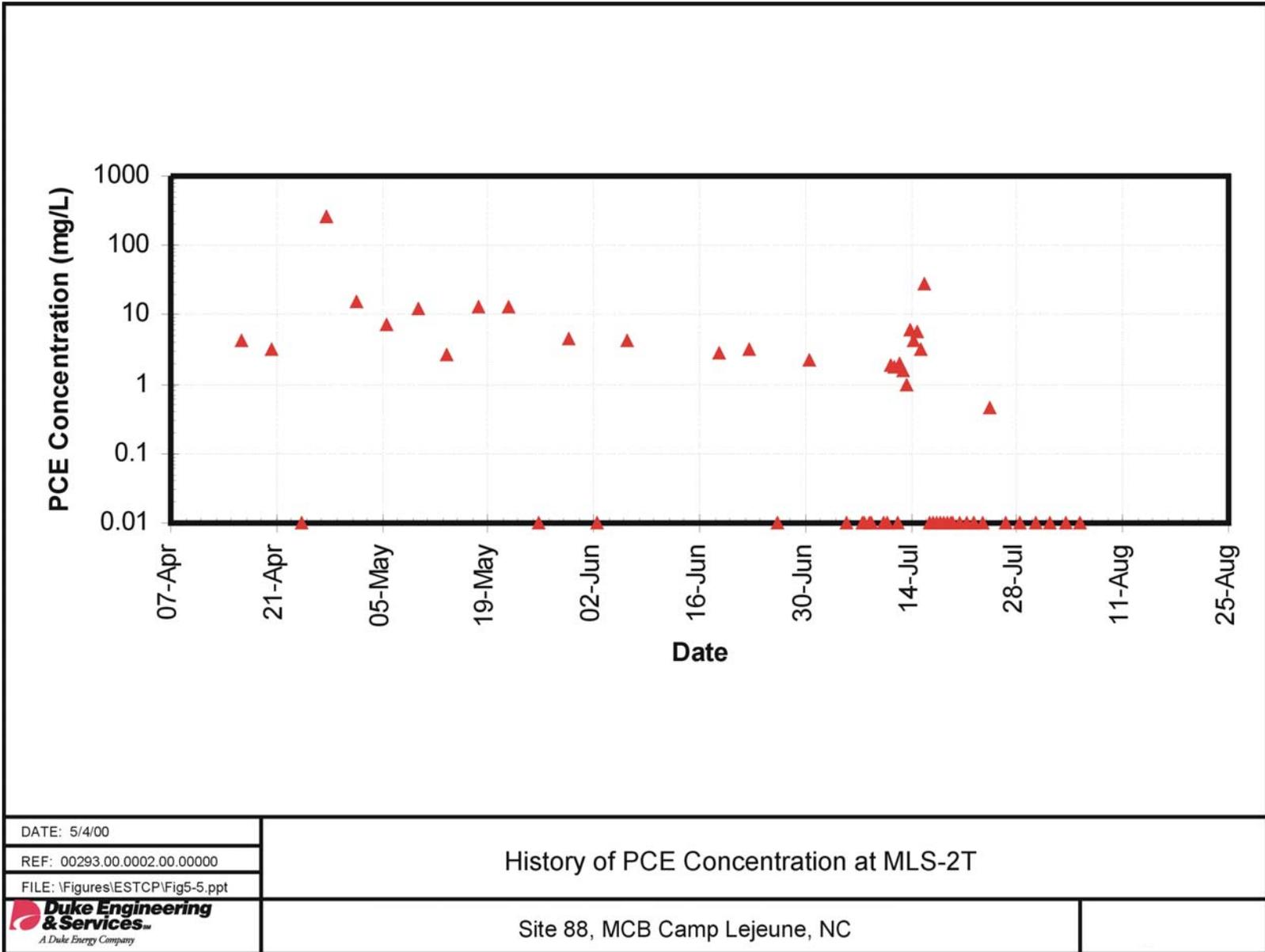
Figure 5-5. History of PCE Concentrations at MLS-2T
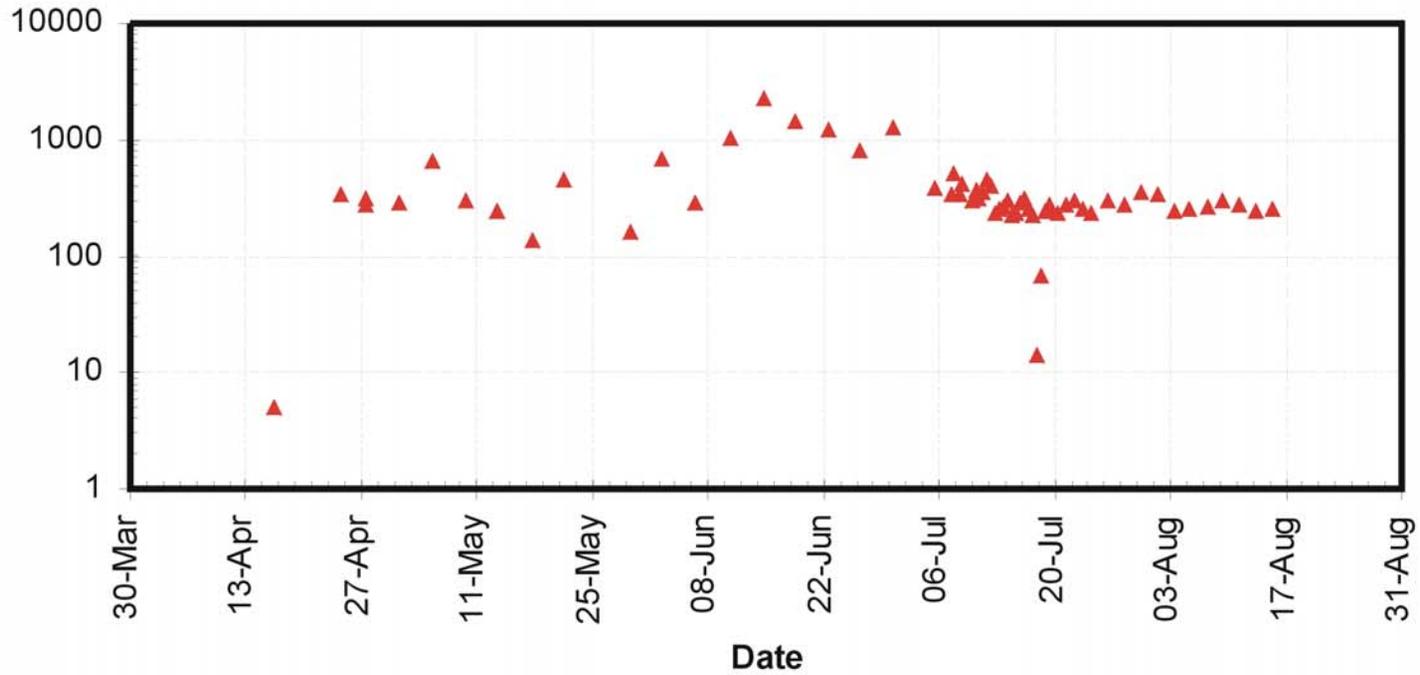
DATE: 5/4/00	
REF: 00293.00.0002.00.00000	History of PCE Concentration at MLS-2M
FILE: \Figures\ESTCP\Fig5-6.ppt	
Duke Engineering & Services SM *A Duke Energy Company*	Site 88, MCB Camp Lejeune, NC	

Figure 5-6. History of PCE Concentrations at MLS-2M
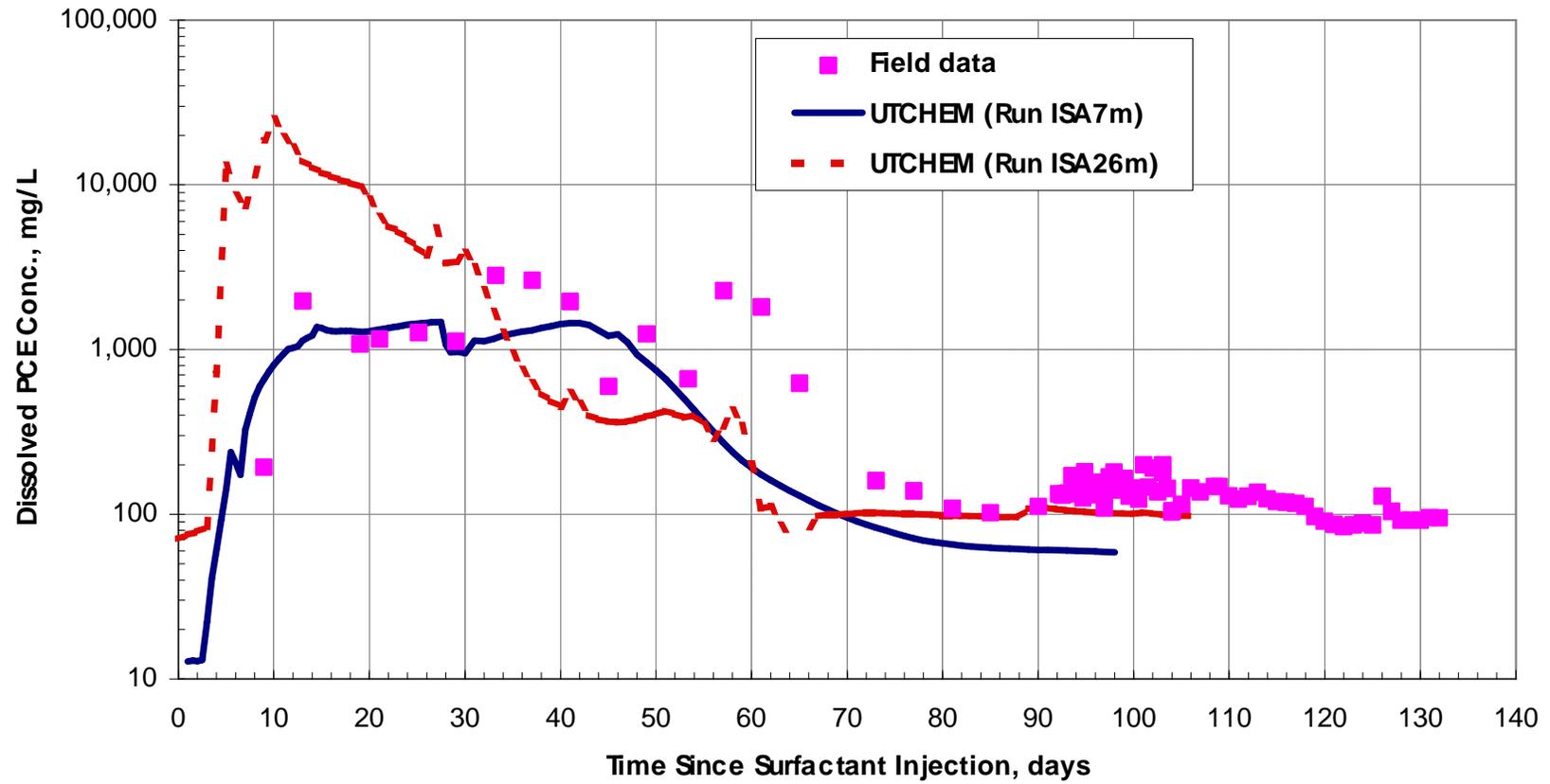
Figure 5-7. Comparison of Predicted and Field Dissolved PCE Concentrations from EX01
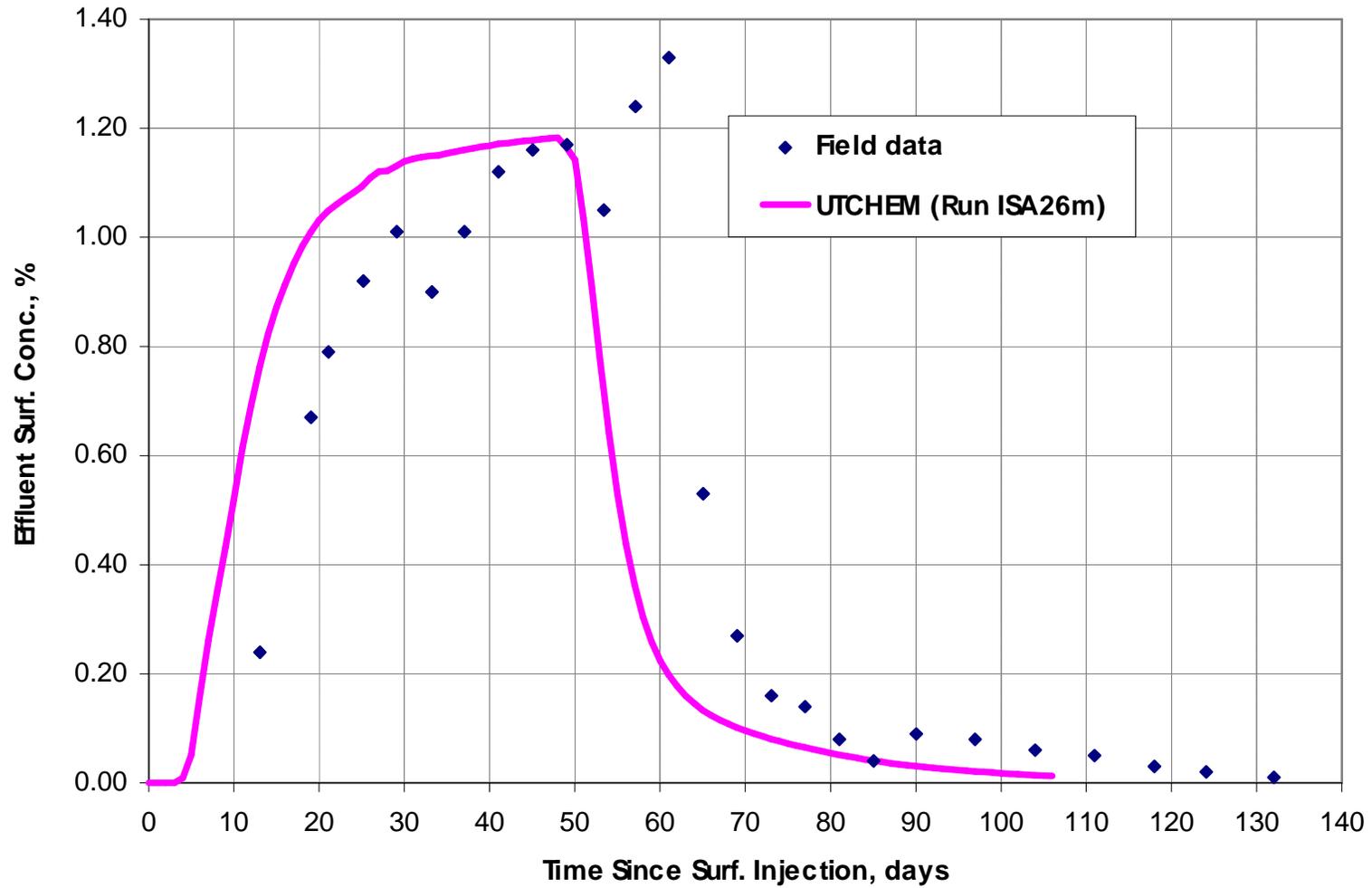
Figure 5-8. Comparison of Predicted and Field Surfactant Concentrations From EX01
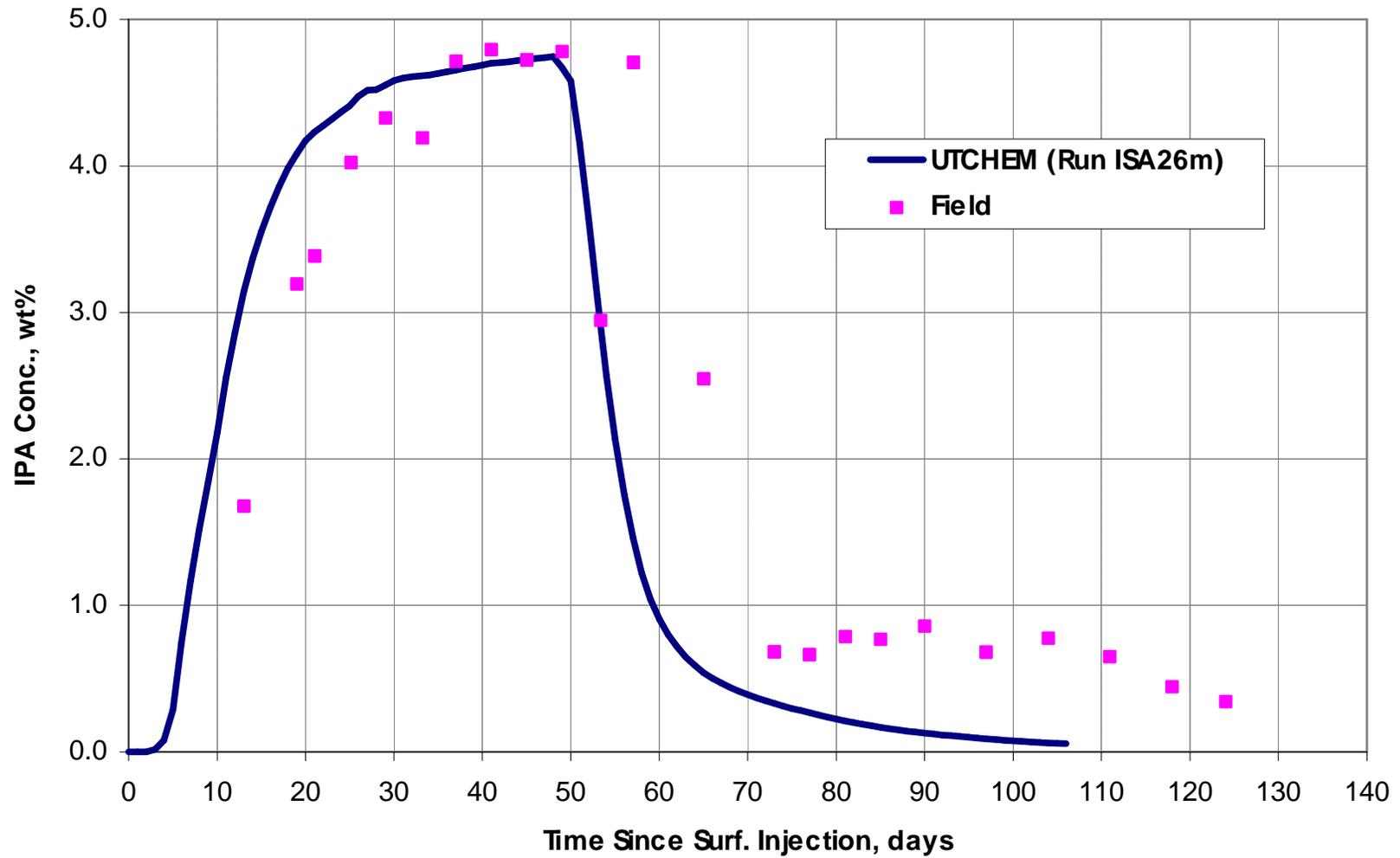
Figure 5-9. Comparison of Predicted and Field IPA Concentrations From EX01

The MLS data for the surfactant and IPA response curves showed that little surfactant injectate penetrated (i.e., swept) the lower-permeability silt layers compared to the more permeable upper zones, as shown in Figures 5-10 and 5-11. Thus, little DNAPL was removed at these lower depths. This result can be attributed primarily to the preferential flow of surfactant injectate through the more permeable upper zones and consequential bypassing of the lower zones, and secondarily to some surfactant sorption and/or biodegradation. This conclusion is reached because recovery of surfactant and IPA chemicals was fairly high (i.e., 78% and 88%, respectively); therefore, surfactant loss would not be the main factor for poor DNAPL removal in the bottom layer. However, surfactant recovery was lower relative to IPA recovery, and some late-time separation between normalized surfactant and IPA curves exists, indicateing that there was some surfactant loss relative to IPA during the latter stages of the SEAR demonstration. Normalized surfactant and IPA curves for EX01, EX02 and EX04R, showing curve separation after 75 days, are provided in Figure 5-12.

In addition to enhancing the solubility of the DNAPL, the surfactant flood also enhanced the recovery of free-phase DNAPL as a result of lowering the IFT of the DNAPL. The IFT of the DNAPL-microemulsion formed in the presence of the surfactant injectate solution was on the order of 0.002 dynes/cm. Due to this low IFT, it is expected that the sum of the viscous and advective forces exceeded the capillary forces trapping DNAPL, thereby causing induced mobilization. Although an IFT of 0.001dynes/cm will generally cause mobilization, the IFT value is a function of a dimensionless quantity called the trapping number and must be computed on a site-by-site basis. Because of the presence of a thick aquitard at the site and because of its greater mass removal efficiency, mobilization of DNAPL during the surfactant flood was desirable and intended by design. A total of 76 gal (288 L) of PCE was recovered during the surfactant flood and subsequent water flood, of which approximately 32 gal (121 L) of PCE were recovered as solubilized DNAPL and 44 gal (167 L) as mobilized free-phase DNAPL. A table showing the volume of solubilized and free-phase DNAPL recovered per well is provided as Table 5-1.

Table 5-1. Recovery of Solubilized and Mobilized PCE from Camp Lejeune Wells

Extraction Well	Solubilized PCE Recovered (gal)	Mobilized PCE Recovered (gal)
EX01	19.4	15.3
EX02	1.9	8.7
EX03	0.1	0.0
EX04	NS	3.6
EX04R	9.4	5.2
EX05	0.9	2.6
EX06	0.1	0.0
RW01	NS	2.0
RW02	NS	2.0
Other sources	0.0	4.6
Total	31.8	44.0

NS: not sampled, PCE concentration data was only collected at the extraction wells.
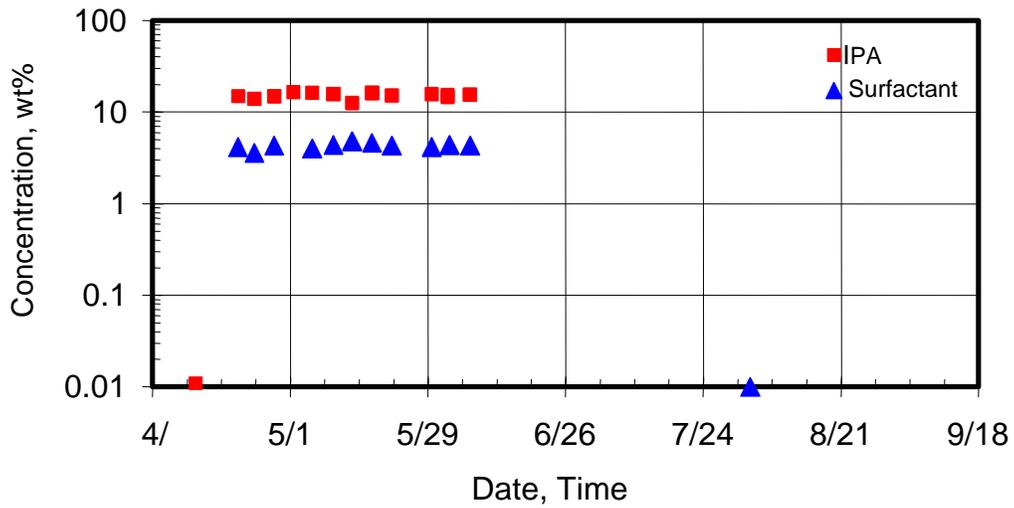
a. History of IPA and Surfactant Concentrations at MLS-4T
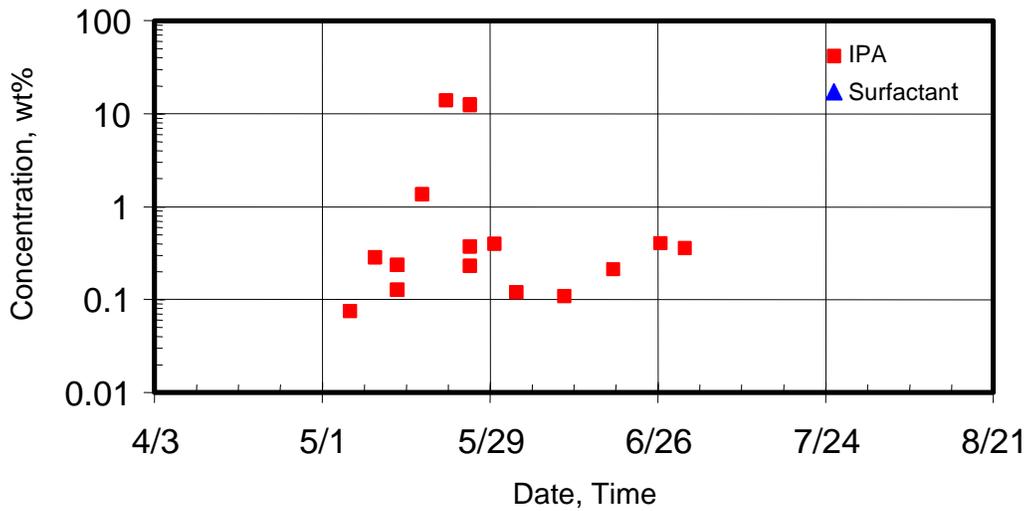
b. History of IPA and Surfactant Concentrations at MLS-4B

DATE:6/26/01	History of IPA and Surfactant Concentrations at MLS-4T and MLS-4B
REF: 0001	
FILE:FTRFIGURES001.PPT	
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Figure 5-10. History of Surfactant and IPA Concentrations at MLS-4T and MLS-4B
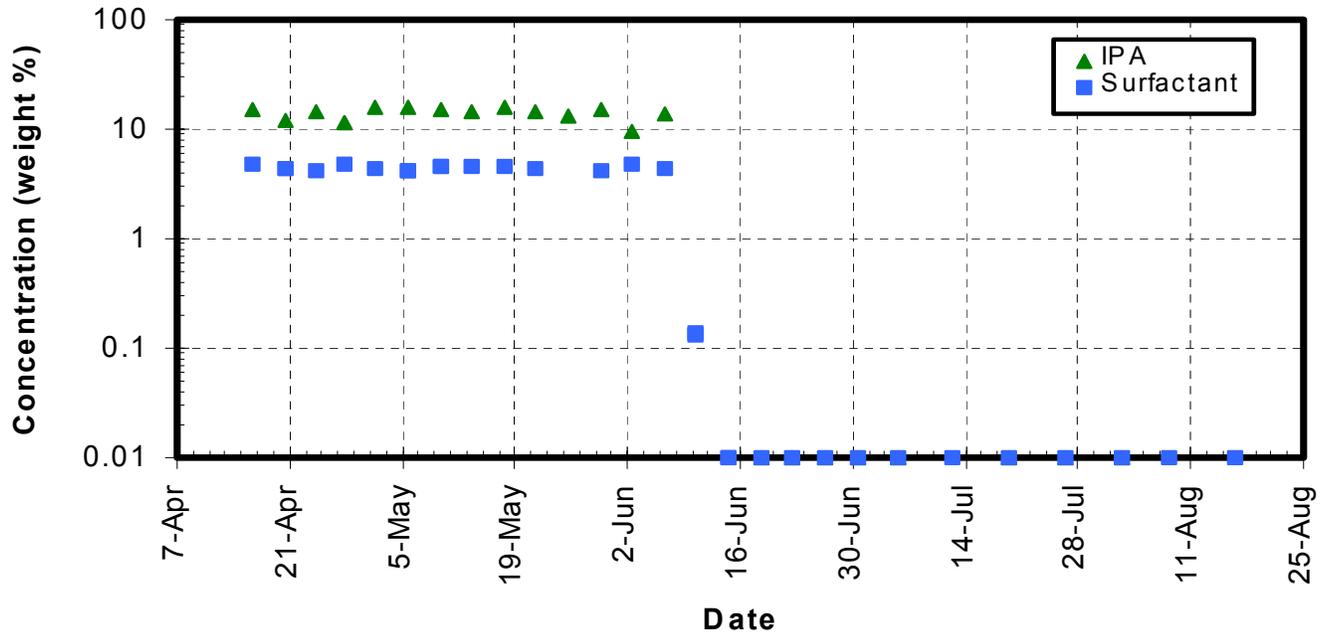
a. History of IPA and Surfactant concentrations at MLS-2T
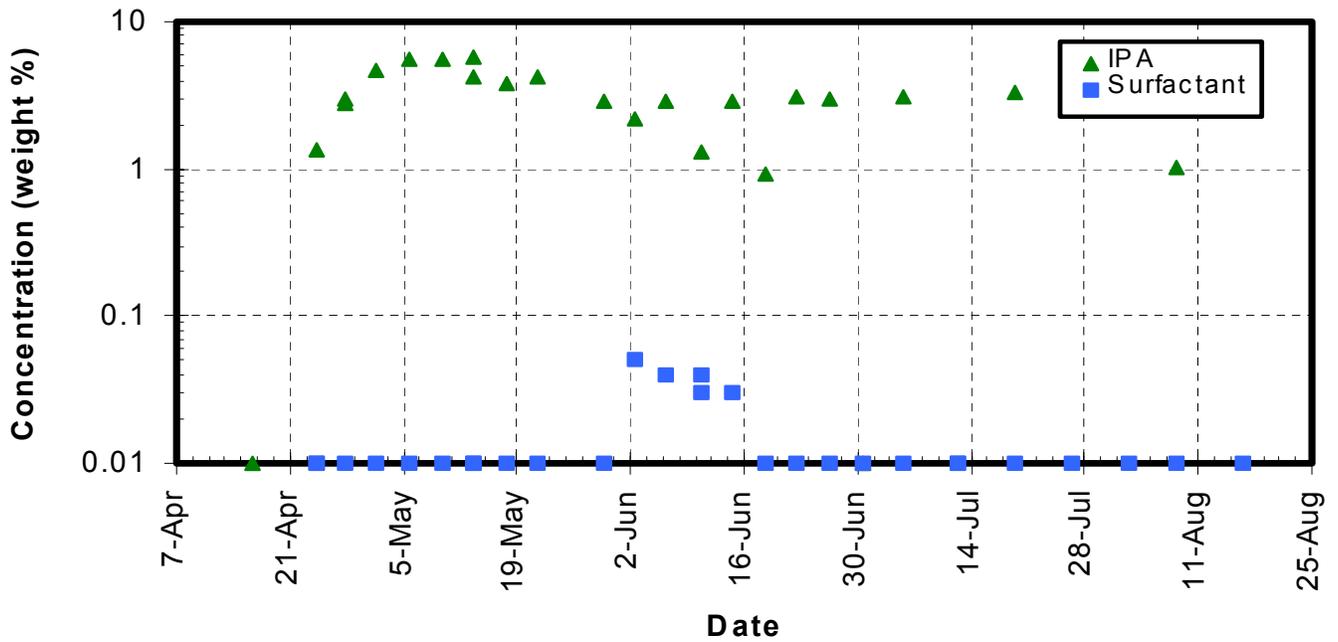
b. History of IPA and Surfactant concentrations at MLS-2M

Figure 5-11. History of Surfactant and IPA Concentrations at MLS-2T and MLS-2M
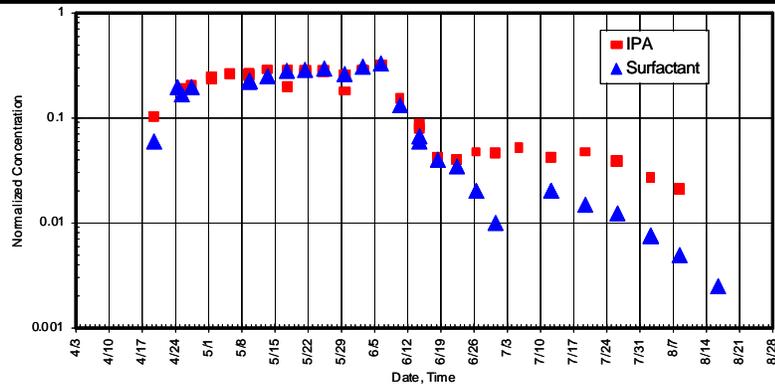
a. Normalized Effluent Concentration History of IPA and Surfactant at Extraction Well EX01
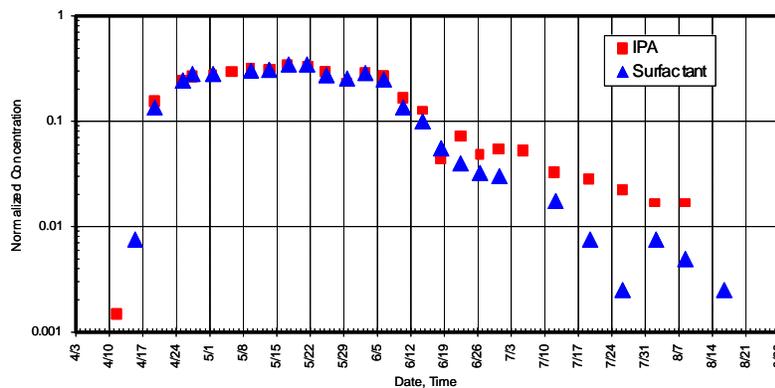
b. Normalized Effluent Concentration History of IPA and Surfactant at Extraction Well EX02
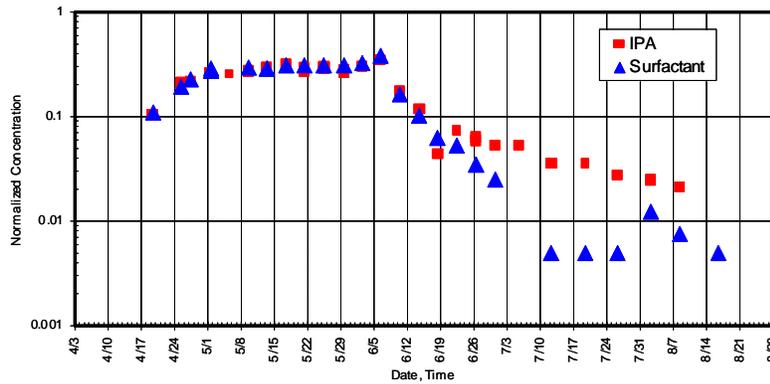
c. Normalized Effluent Concentration History of IPA and Surfactant at Extraction Well EX04

DATE: 5/4/00	Normalized Effluent Concentration History of IPA and Surfactant at Extraction Wells EX01, EX02 and EX04	
REF: 00293.00.0002.00.00000		
FILE: \Figures\ESTCP\Fig5-12.ppt		
Duke Engineering & Services. A Duke Energy Company	Site 88, MCB Camp Lejeune, NC	Figure 5-12

Figure 5-12. Normalized Effluent Concentration History of IPA and Surfactant at EX01, EX02, and EX04R

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Potentiometric surface maps of the shallow aquifer generated for several phases of the demonstration show that hydraulic control of injected fluids was effectively maintained, with the exception of a minor loss of hydraulic control at HC01 during Phase II of the surfactant flood (see Table 4-1 for identification of test phases). This loss was caused by a slightly exaggerated gradient between injection well IN01 and HC01 with the higher viscosity surfactant fluids. This temporary loss of hydraulic control was confirmed by increasing IPA concentrations with time at monitoring well RW03, peaking on July 27 (Day 112 of the test) at 2,798 mg/L (compare to IPA injectate concentration = 160,000 mg/L). However, recovery of 88% of the injected IPA by the end of the demonstration suggests that any loss of hydraulic control was very minor. During the post-SEAR water flood and post-SEAR PITT, the potentiometric surface maps show that hydraulic containment was fully established and maintained for the remainder of the demonstration. In support of this, IPA concentrations at well RW03 dropped to 428 mg/L with the last monitoring sample collected on August 27. Potentiometric surface maps assembled during various phases of flooding operations can be viewed in Appendix D. Monitoring well data can be viewed in Appendix E. The samples collected from these wells show that in addition to good hydraulic control, there was no undesired vertical mobilization of contaminant due to surfactant flooding.

Residual surfactant and IPA remaining in the ground following SEAR treatment were not a concern for further transport of residual and dissolved-phase contamination to uncontaminated regions of the aquifer. Surfactants cause ultralow interfacial tensions only under optimal salinity conditions (i.e., high electrolyte concentrations). For the surfactant formulation used at Camp Lejeune, approximately 1,800 mg/L calcium chloride was required to produce ultralow interfacial tensions for high contaminant solubilization and to induce DNAPL mobilization. During the postsurfactant water flood, 1,000 mg/L calcium chloride was injected, which reduced electrolyte concentrations in the aquifer. Such conditions are consistent with a Winsor type I phase behavior, which results in relatively high interfacial tensions that will limit enhanced solubilization and mobilization. Furthermore, the Camp Lejeune surfactant is biodegradable. Post-SEAR GW monitoring (see Section 5.1.3) suggests resumption of biological activity as evidenced by the formation of acetone from IPA. It is expected that residual surfactant and IPA will be biodegraded and thus not be a mechanism for further transport of the contaminants. Furthermore, residual surfactant may enhance the biopolishing process.

The post-SEAR PITT was conducted, along with soil core sampling, to measure the volume of DNAPL remaining in the test zone after the surfactant flood. The results of the post-SEAR PITT, however, proved to be unusable due to interference with a minor component of the surfactant that sorbed to the aquifer. These post-SEAR PITT results will not be discussed further here as they are not used for evaluating SEAR performance; presentation of this data may be found in the SEAR Final Report (DE&S, 2000). All soil samples collected for analysis of VOCs were field preserved with methanol.

The post-SEAR soil sampling data consisted of 60 soil samples collected at 12 locations over the contaminated portion of the aquifer, and was used to generate a three-dimensional distribution of the DNAPL volume remaining in the test zone following the surfactant flood. Sampling locations are shown in Figure 5-13. Continuous cores were collected from the bottom 3 feet of the aquifer (representing the DNAPL treated zone) and then subdivided into 6-inch core samples. Although it was intended to recover up to 4 feet of the core at each sampling location, in most instances only 2.5 to 3 feet of core could be recovered. The post-SEAR soil PCE concentrations and DNAPL saturations are shown in Table 5-2, while a graphical representation of this data is provided in Figure 5-14. The lateral distribution of DNAPL indicates that the majority of the DNAPL that remains in the test zone is located near the building, between wells EX01 and EX04. DNAPL volume decreases away from the building, in the area between wells EX02 and EX05, and very little DNAPL is present in the portion of the test zone that is farthest from the building, between wells EX03 and EX06. The vertical distribution of remaining
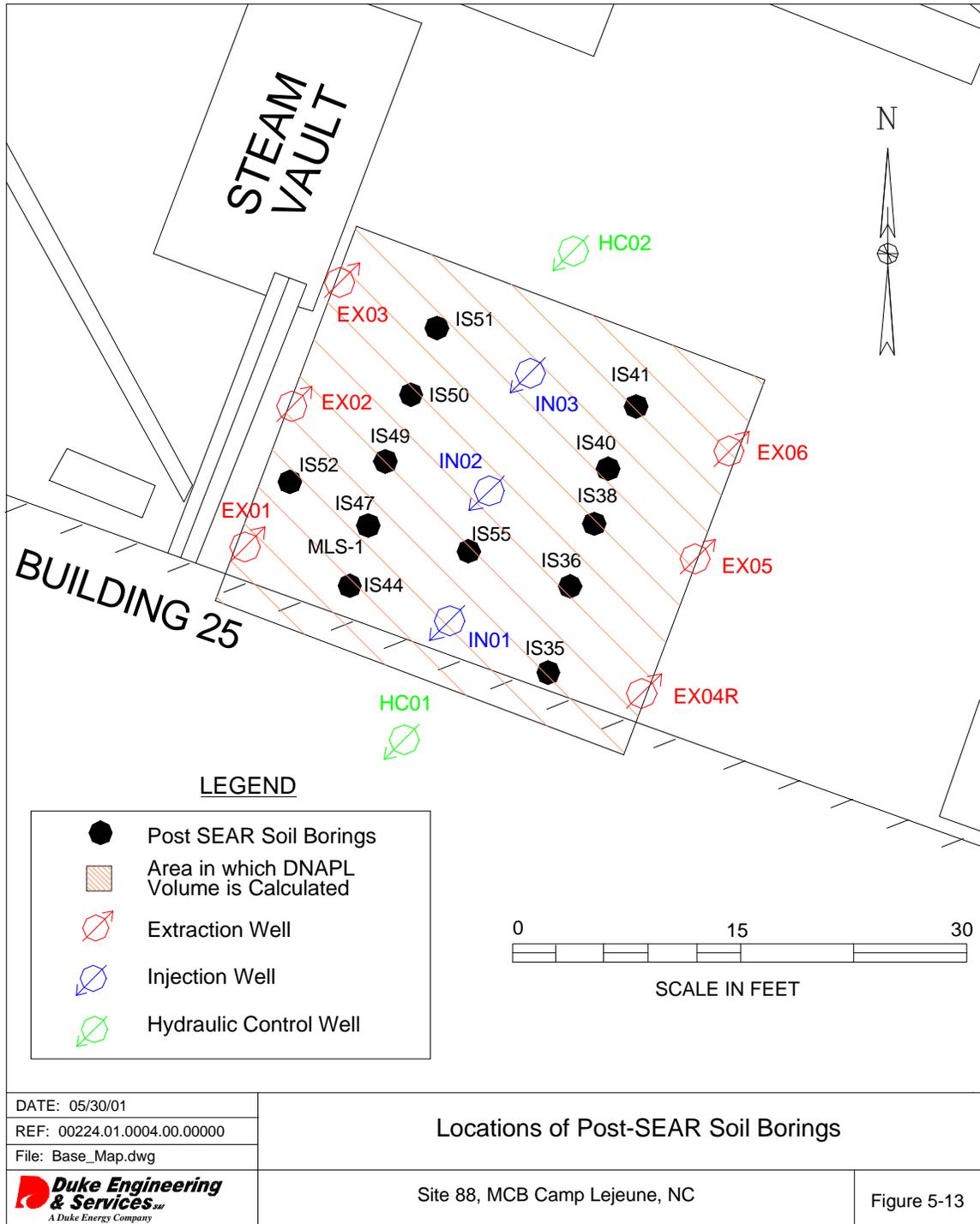
Figure 5-13. Post-SEAR Soil Boring Locations at Site 88, MCB Camp Lejeune, NC

Table 5-2. Post-SEAR Soil PCE Concentrations and DNAPL Saturations

Post-SEAR Boring ID	Soil Sample Depth (ft bgs)	f_{oc} [a]	PCE Concentration (mg/kg in wet soil)	DNAPL Saturation (%)
IS35-2	17.0-17.5	0.0023	2.1	0.0
IS35-3	17.5-18.0	0.0023	2,533	0.7
IS35-4	18.0-18.5	0.0084	6,247	1.7
IS35-5	18.5-19.0	0.0084	11,129	3.2
IS35-6	19.0-19.5	0.0084	1,084	0.1
IS36-2	17.0-17.5	0.0023	3,088	0.9
IS36-3	17.5-18.0	0.0023	9,655	2.9
IS36-4	18.0-18.5	0.0084	3,887	1.0
IS36-5	18.5-19.0	0.0084	3,549	0.9
IS36-6	19.0-19.5	0.0084	485	0.0
IS38-3	17.5-18.0	0.0023	0.2	0.0
IS38-4	18.0-18.5	0.0084	ND	0.0
IS38-5	18.5-19.0	0.0084	1,471	0.3
IS38-6	19.0-19.5	0.0084	11,810	3.4
IS40-2	16.5-17.0	0.0023	ND	0.0
IS40-3	17.0-17.5	0.0023	ND	0.0
IS40-4	17.5-18.0	0.0023	ND	0.0
IS40-5	18.0-18.5	0.0084	144	0.0
IS40-6	18.5-19.0	0.0084	1,692	0.3
IS41-1	16.5-17.0	0.0023	ND	0.0
IS41-2	17.0-17.5	0.0023	ND	0.0
IS41-3	17.5-18.0	0.0023	ND	0.0
IS41-4	18.0-18.5	0.0084	30	0.0
IS41-5	18.5-19.0	0.0084	1.5	0.0
IS41-6	19.0-19.5	0.0084	0.5	0.0
IS44-2	17.0-17.5	0.0023	57	0.0
IS44-3	17.5-18.0	0.0023	9,759	2.9
IS44-4	18.0-18.5	0.0084	6,142	1.7
IS44-5	18.5-19.0	0.0084	8,754	2.5
IS44-6	19.0-19.5	0.0084	739	Trace
IS47-2	17.5-18.0	0.0023	8,279	2.5
IS47-3	18.0-18.5	0.0084	5,839	1.6
IS47-4	18.5-19.0	0.0084	5,587	1.5
IS47-5	19.0-19.5	0.0084	7,651	2.2
IS47-6	19.5-20.0	0.0084	7,536	2.1
IS49-1	17.0-17.5	0.0023	1.7	0.0
IS49-2	17.5-18.0	0.0023	1.3	0.0
IS49-3	18.0-18.5	0.0084	6,144	1.7
IS49-4	18.5-19.0	0.0084	4,689	1.2
IS49-5	19.0-19.5	0.0084	17,198	5.1
IS49-6	19.5-20.0	0.0084	4,268	1.1
IS50-1	17.0-17.5	0.0023	ND	0.0
IS50-2	17.5-18.0	0.0023	ND	0.0
IS50-3	18.0-18.5	0.0084	3,159	0.8
IS50-4	18.5-19.0	0.0084	5,147	1.4
IS50-5	19.0-19.5	0.0084	7,382	2.1
IS50-6	19.5-20.0	0.0084	3,182	0.8

Table 5-2. Post-SEAR Soil PCE Concentrations and DNAPL Saturations (Continued)

Post-SEAR Boring ID	Soil Sample Depth (ft bgs)	f_{oc} [a]	PCE Concentration (mg/kg in wet soil)	DNAPL Saturation (%)
IS51-1	17.0-17.5	0.0023	ND	0.0
IS51-2	17.5-18.0	0.0023	20	0.0
IS51-3	18.0-18.5	0.0023	181	0.0
IS51-4	18.5-19.0	0.0084	2,930	0.7
IS51-5	19.0-19.5	0.0084	338	0.0
IS51-6	19.5-20.0	0.0084	85	0.0
IS52-2	17.5-18.0	0.0023	3,432	1.0
IS52-3	18.0-18.5	0.0084	5,997	1.6
IS52-4	18.5-19.0	0.0084	5,813	1.6
IS52-5	19.0-19.5	0.0084	3,926	1.0
IS55-2	17.5-18.0	0.0023	3,077	0.9
IS55-4	18.5-19.0	0.0084	5,134	1.4
IS55-5	19.0-19.5	0.0084	1,847	0.4

(a) Fraction of sedimentary organic carbon in aquifer material (wt/wt)

DNAPL indicates that DNAPL was effectively removed from the more permeable sediments, generally above about 17.5 ft (5.3 m) bgs, and that DNAPL still remains in the lower permeability basal silt layer. These results are consistent with the fact that the highest pre-SEAR DNAPL saturations were near the building. The results also demonstrate the difficulty experienced in removing DNAPL from the lowest permeability sediments at the site.

Following the SEAR demonstration, efforts were made to better understand the permeability variation over the DNAPL contaminated zone. Grain size analyses were conducted on the 60 post-SEAR soil samples that were collected to measure the DNAPL saturations, as well as an additional 12 soil samples that were collected from the contaminated zone for grain size analyses only. The "effective" grain diameters (d_e) obtained were correlated to permeability (k) using the following relationship: $k \propto d_e^2$ This permitted observation of the trend in permeability with depth. The results of this analysis are shown in semilog plot in Figure 5-15. This shows a clearly decreasing trend in permeability between 16.5 to 20 ft bgs of up to two orders of magnitude. For a complete discussion on the correlation of grain size to permeability, see Section 9 of the SEAR Final Report (DE&S, 2000) in Appendix G.

Simultaneous with the grain-size investigations, a preliminary effort was made to history match the results from numerical simulations with the observed field data. A history match involves varying the parameters of the numerical model used to design the SEAR test, to look for a best fit to the field data. This achieves better understanding of the actual conditions encountered in the field by calibrating the model to the observed field data. This demonstrated that the best match of the field data is achieved by using a three-layer permeability system in the model rather than the two-layer system that was originally used to design the SEAR test. The three-layer system is consistent with the gradational trend of decreasing permeability with depth in the basal portion of the aquifer, as shown by the grain-size analyses. In this history match, the actual flowrates employed during the SEAR demonstration were used (see Table 4-1). The permeability and initial DNAPL saturation parameters used for the history match simulation, compared against those used for ISA7m and ISA26m, are provided in Table 5-3. The results of the history match for EX01 are provided in Figures 5-16, 5-17 and 5-18. These may be compared to the original design simulations, ISA26m, provided earlier in Figures 5-7, 5-8 and 5-9.
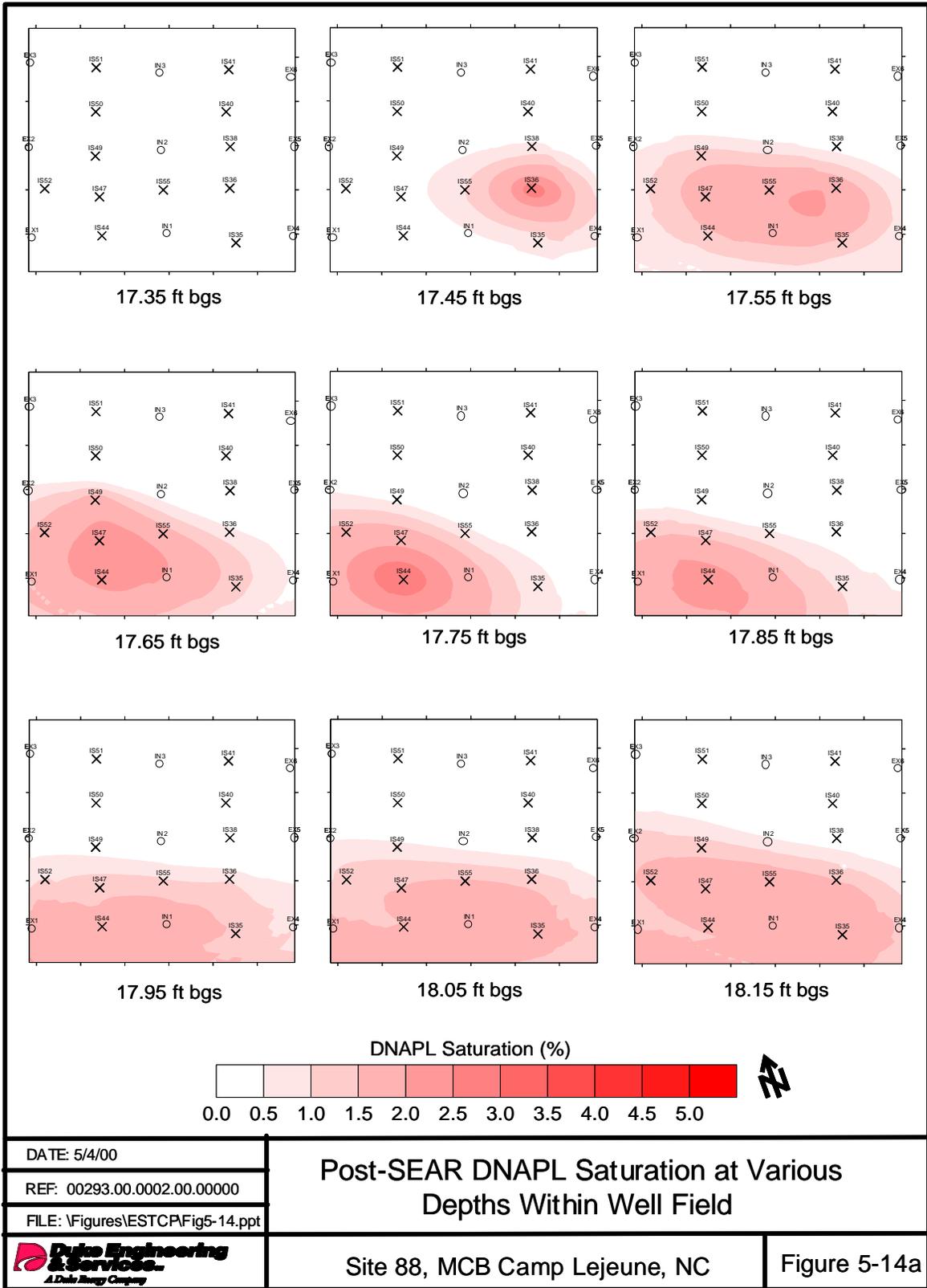
Figure 5-14a. Post-SEAR DNAPL Saturations at Various Depths Within the Well Field at Site 88, MCB Camp Lejeune, NC
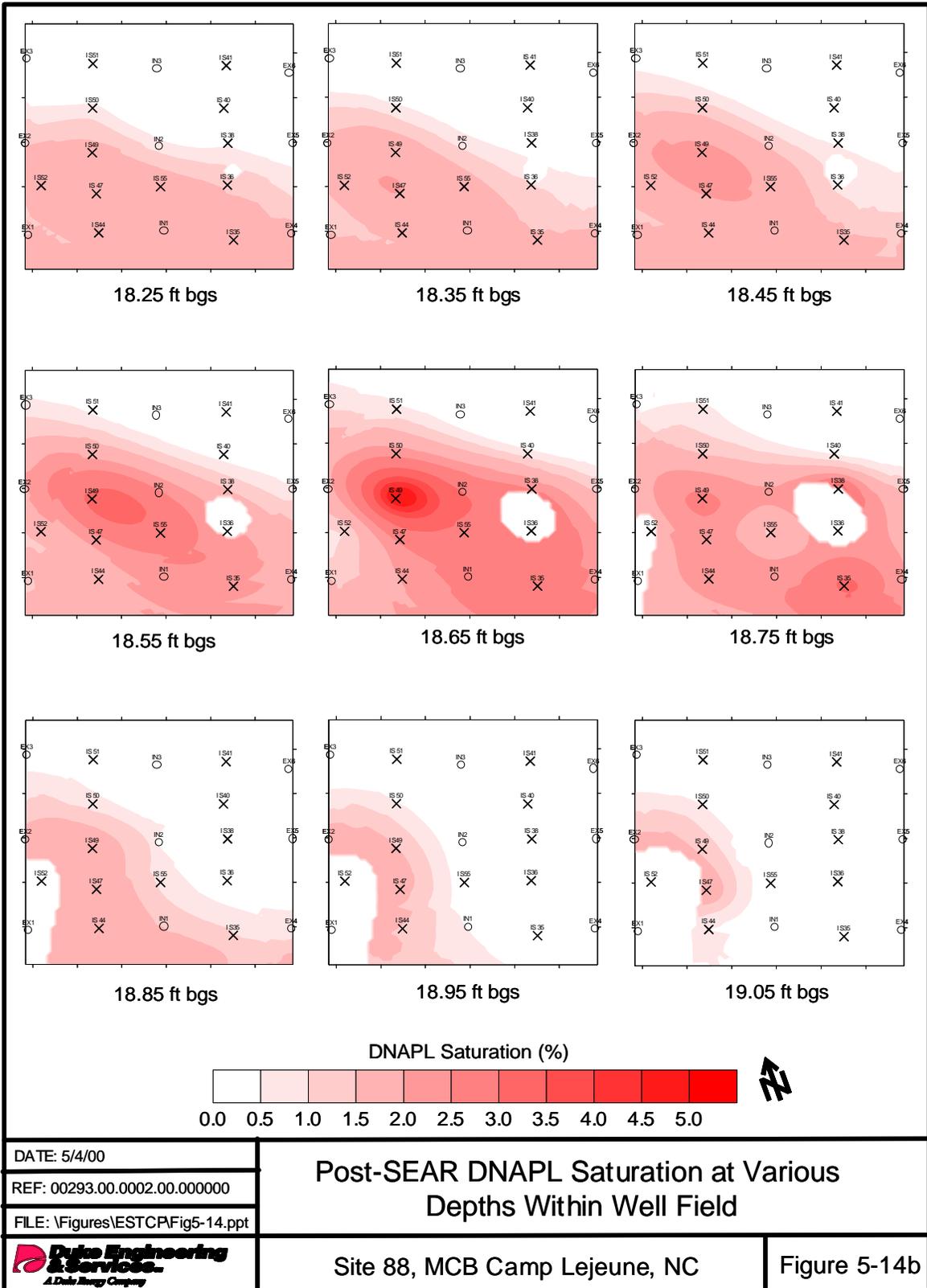
Figure 5-14b. Post-SEAR DNAPL Saturations at Various Depths Within the Well Field at Site 88, MCB Camp Lejeune, NC
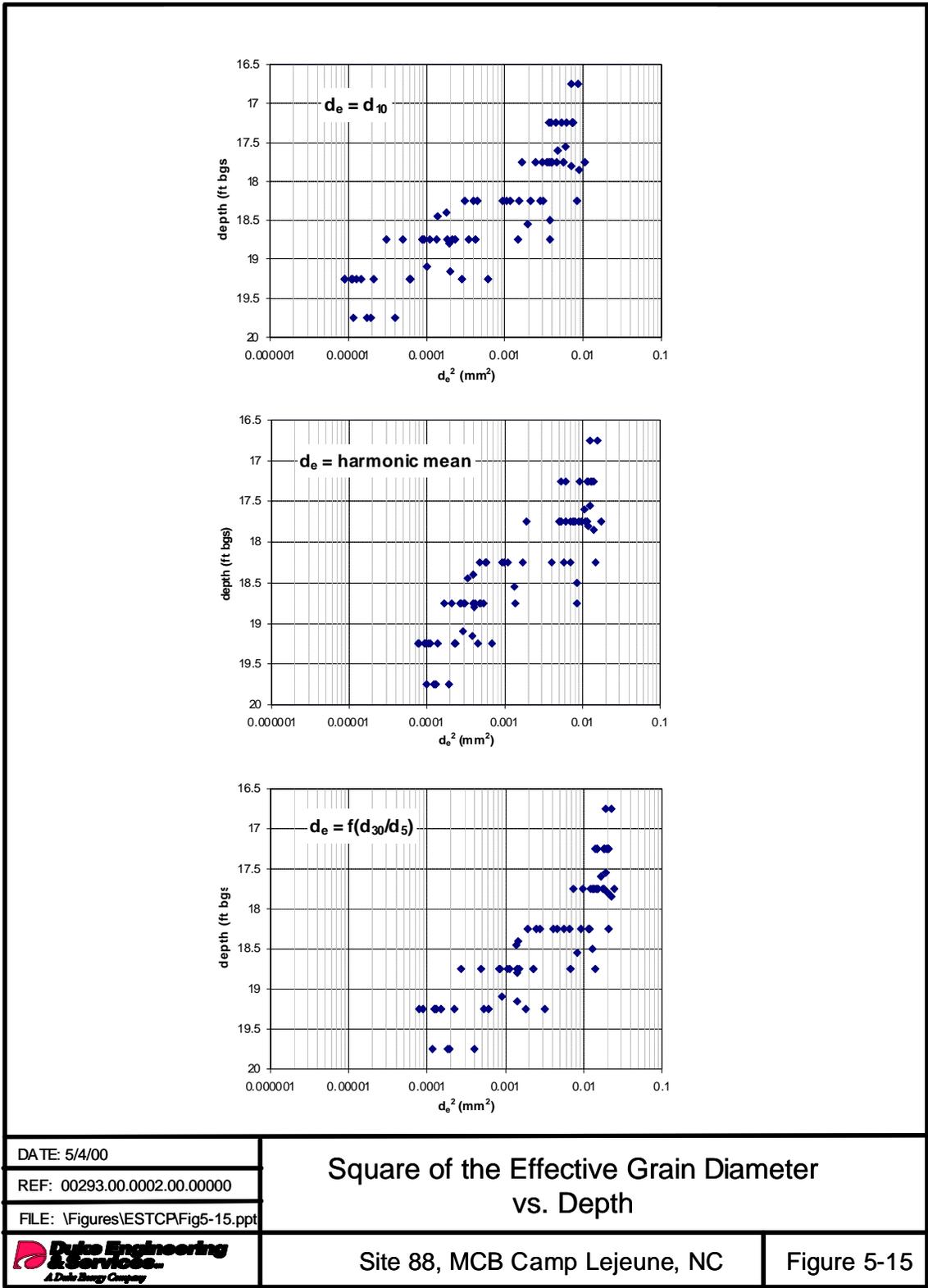
Figure 5-15. Square of the Effective Grain Diameter Versus Depth at Site 88, MCB Camp Lejeune, NC
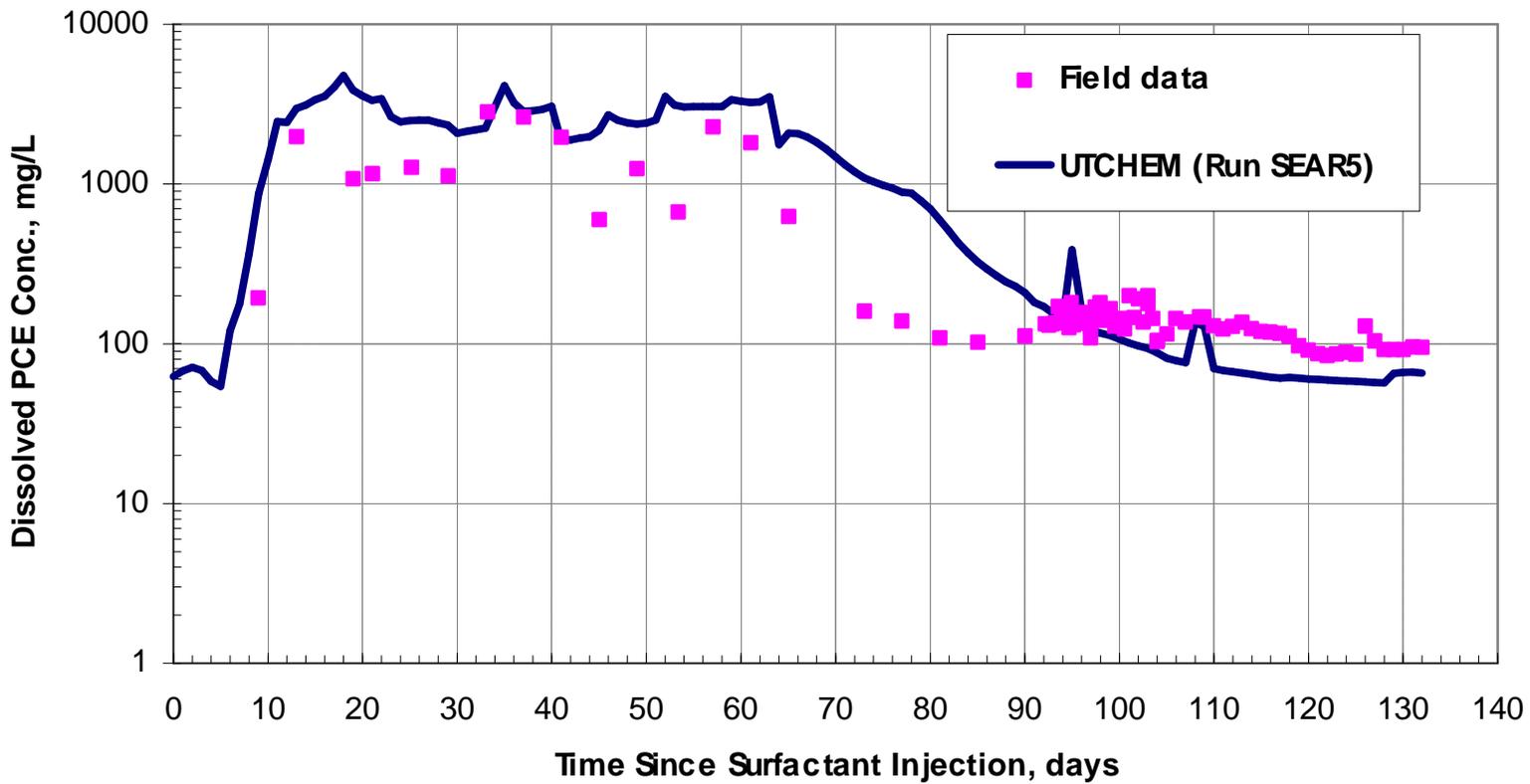
Figure 5-16. Comparison of Field and History Match Simulation Result of PCE Concentration for EX01
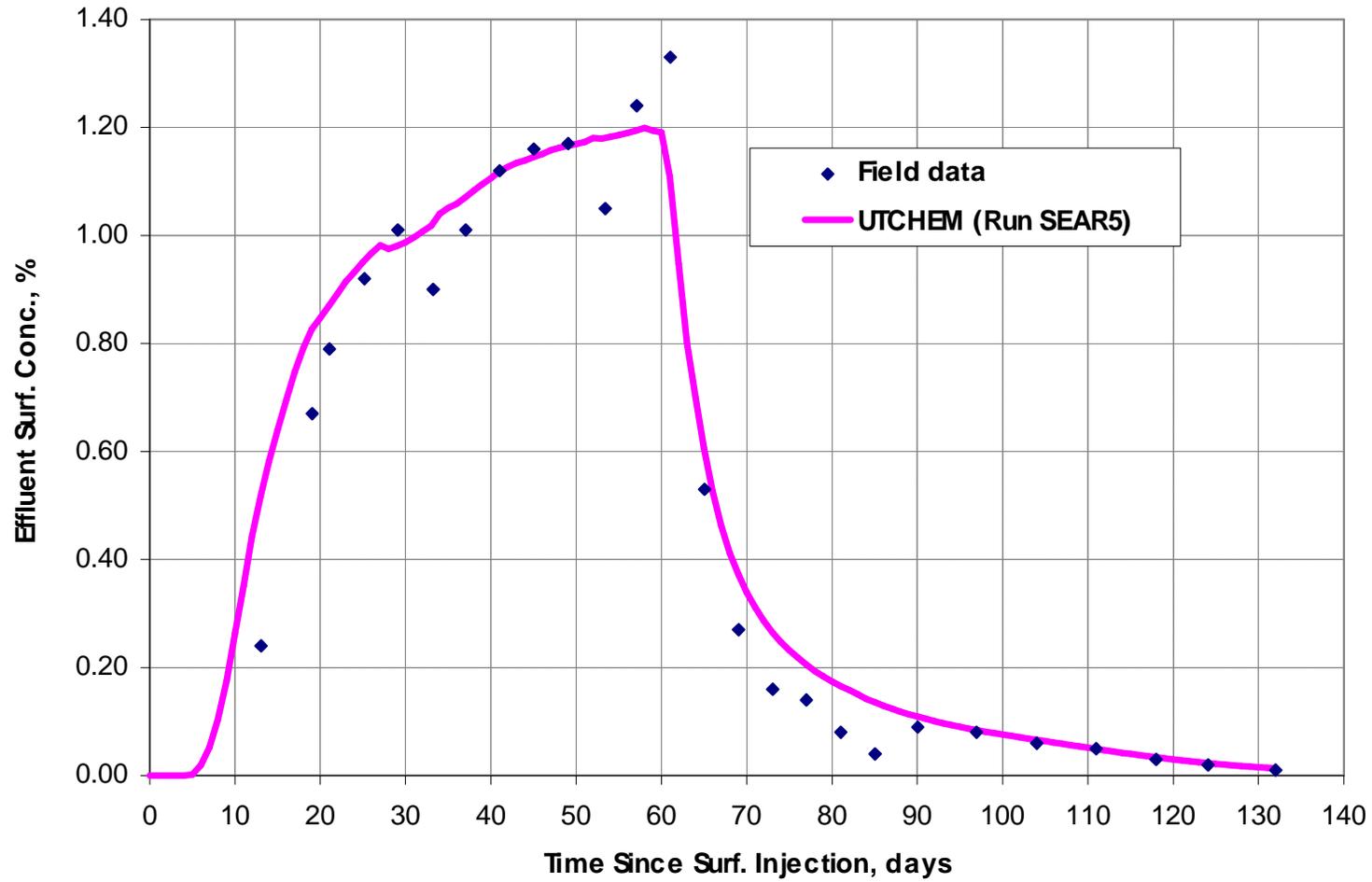
Figure 5-17. Comparison of Field and History Match Simulation Result of Surfactant Concentration for EX01
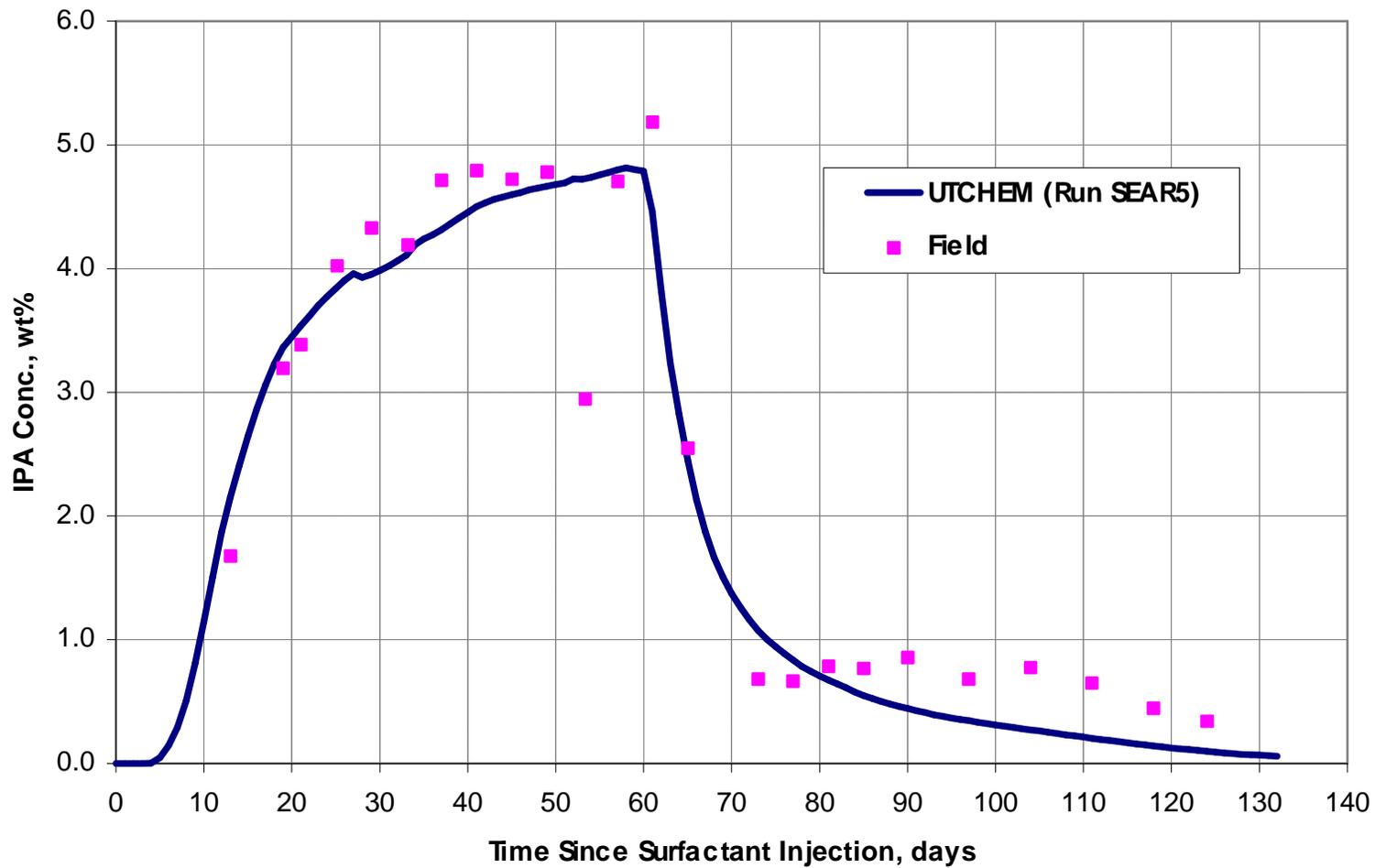
Figure 5-18. Comparison of Field and History Match Simulation Result of IPA Concentration for EX01

Table 5-3. Parameters Used for the History Match, ISA7m, and ISA26m Simulations

Variable	History Match (post-SEAR)	ISA7m (Preliminary Simulation)	ISA26m (used for SEAR Design)
Permeability[a]	Layers 1 to 12 (11 ft): 200 md Layers 13-14 (1 ft): 50 md Layers 15-16: (1 ft): 10 md	Layers 1 to 12 (11 ft): 400 md Layers 13-16 (2 ft): 80 md	Layers 1 to 14 (12 ft): 400 md Layers 15-16 (1 ft): 100 md
Initial DNAPL saturation	Layer 12: 0.05, north of IN02: 0.00 Layer 13: 0.075, north of IN02: 0.00 Layer 14: 0.15, north of IN02: 0.00 Layer 15: 0.2, north of IN01: 0.00 Layer 16: 0.2, north of IN01 and west of EX04R: 0.00	Layer 13: 0.02 Layer 14: 0.1 Layer 15: 0.15 Layer 16: 0.16	Layer 13: 0.075, north of IN02 0.02 Layer 14: 0.1, north of IN02: 0.02 Layer 15: 0.20, north of IN01: 0.00 except for gridblocks between EX02 and MLS-2: 0.20, and EX05 and EX06: 0.20 Layer 16: 0.25, north of IN01 and west of EX04R: 0.00 except for gridblocks surrounding EX05: 0.25
Residual DNAPL Saturation[b]	0.0015	0.0015	0.0016

(a) Permeability is given for vertical layers (z) assuming uniformity in the lateral (x-y) directions. The individual vertical layer thicknesses are as follows: Layers 1-3 (2 ft); Layer 4 (1 ft); Layers 5-16 (0.5 ft)

(b) This is an average value over all contaminated layers.

md = millidarcies

Given the expected permeability contrast of 5:1 prior to the SEAR, the design approach used to remediate the basal silt layer was to increase the number of surfactant flood pore volumes from three to five in order to sweep the low-permeability zone. This decision was supported by design simulations that indicated an effective sweep under these hydrogeologic conditions could be met with a 5-pore volume surfactant flood. The results of the SEAR demonstration showed that this design did effectively remediate the upper portions of the basal silt layer where the permeability contrast range is about 3:1 to 5:1. However, the design was unable to accommodate the greater permeability contrast that actually existed in the lowest portion of the aquifer. Based on lessons learned, for a robust SEAR design, it is necessary to consider mobility control measures that can overcome the tendency of SEAR fluids to preferentially flow through zones of higher permeability in a heterogeneous aquifer.

5.1.2   SEAR Effluent Treatment and Surfactant Recovery. The aboveground SEAR effluent treatment processes, pervaporation and ultrafiltration, operated for more than two months to recover surfactant from the extraction well effluent (containing surfactant and solubilized DNAPL) for reinjection into the aquifer. The combined extraction well effluent averaged 1 gpm and contained a maximum of 900 mg/L PCE, 1.2 wt% surfactant, and 4.1 wt% IPA at peak breakthrough. Only limited membrane fouling was observed despite high concentrations of iron (14 mg/L Fe^{2+}) and calcium (300 mg/L Ca^{2+}). The overall objective of recovering surfactant with characteristics acceptable for reinjection

was accomplished, which required an average 95% contaminant removal from the extracted surfactant solution and reconcentration of subsurface-diluted surfactants to a minimum of 4.5 wt%. Pervaporation accomplished the 95% removal objective for PCE (see Figure 5-19). Whether pervaporation achieved 95% removal for the secondary contaminant, Varsol™, when averaged over the operational period (before and after surfactant breakthrough) is difficult to evaluate. This is due to the exceedingly low concentrations of Varsol™ extracted from the well field. However, there is sufficient data for two of the three Varsol™ marker compounds to indicate that, in the presence of surfactant, decane removal averaged 56% and undecane removal averaged 33%. The poorer performance of pervaporation for these hydrophobic semivolatile compounds was expected because of their high affinity for the surfactant micelles, and indicates that alternative technologies must be considered if the removal of semi- and nonvolatile compounds from a surfactant solution is a primary objective. As demonstrated on this project, pervaporation is a very viable technology for the removal of volatile compounds from a surfactant solution.

Ultrafiltration achieved or exceeded the desired concentration factor (of 5 on average) necessary to remix the recovered surfactants at design injectate concentrations for reinjection. With the need to replace constituents in the surfactant solution not being recovered in the effluent treatment processes, such as alcohol, it was necessary to minimally concentrate the surfactants to 4.5 wt% for reinjection at their original concentration of 4.0 wt%. The average influent surfactant concentrations from the pervaporation unit to the ultrafiltration unit were 1.1 wt%, whereas the average permeate surfactant concentrations were 0.25 wt%; therefore, surfactant recovery was approximately 77%. Surfactant mass balance calculations performed over the entire volume of processed surfactant result in a similar calculation of approximately 76% surfactant recovery. It is approximately equivalent to 95% recovery of surfactant with each pass over five passes, when the retentate (concentrated surfactant stream) is being recycled to the influent and the permeate (dilute surfactant stream) is being disposed. System pressures were up to twice as high in the field due to slight membrane fouling by iron and humic materials, which caused higher leakage of surfactant across the membrane. At the same time, lower than anticipated surfactant concentrations in the SEAR effluent (1 wt% vs. 1.5 wt% at peak surfactant breakthrough) required a greater number of passes being required to achieve the target surfactant concentration which also increased surfactant losses. Due to operational logistics, surfactants were often concentrated to a higher concentration (e.g., to 5-6 wt%) than necessary. Therefore, although the 76-77% surfactant recovery fell short of the 90% target, it was considered to be within an acceptable range.

The primary issue with UF performance for surfactant reconcentration was the unintended parallel concentration of contaminants and calcium, both of which remained preferentially with the surfactant when water was removed. This is shown in Table 5-4, for the first recycled surfactant batch produced from the UF unit. This represents the most dilute surfactant processed by the UF unit, and it can be seen that to bring surfactants to their final concentration of 5 wt% required a 10-fold concentration factor. Contaminants and calcium were also concentrated by this factor. Although reconcentration of contaminant is a more critical issue for regulatory compliance, the super concentration of calcium poses a greater concern from an operational standpoint. Although the concentration of contaminants during UF processing can be minimized by making the contaminant removal step more efficient, no solutions are readily available for avoiding unacceptably high concentrations of calcium in the surfactant recovered. Excessive calcium concentrations will degrade the performance of most anionic surfactants used in subsurface applications. However, calcium buildup in MEUF will not be an issue for surfactant recovery at all sites. The degree to which MEUF will concentrate the calcium is a function of the surfactant itself. Furthermore, many sites will not require the sole use of calcium as the electrolyte in order to prevent the mobilization of soil fines.
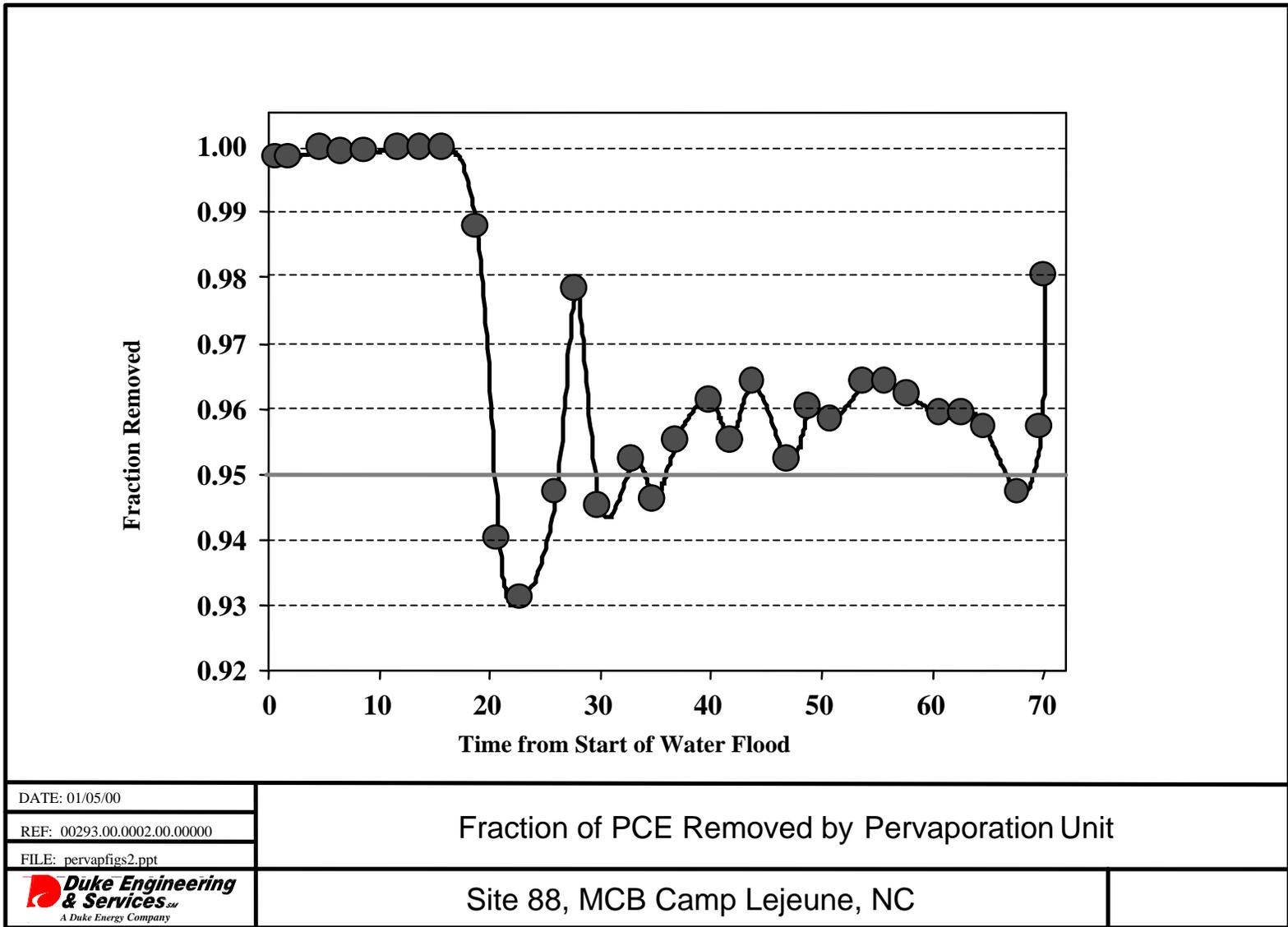
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Fraction of PCE Removed by Pervaporation Unit

Site 88, MCB Camp Lejeune, NC

Figure 5-19. Fraction of PCE Removed by Pervaporation Unit

Table 5-4. Comparison of Pervaporation and MEUF Product Streams

Constituent	Pervaporation	Ultrafiltration
Surfactant	0.95 wt%	5.0 wt%
IPA	3 wt%	3.4 wt%
Calcium	0.03 wt%[a]	0.25 wt%
PCE	28 mg/L	139 mg/L
Decane[b]	0.8-1.25 mg/L	6.4 mg/L
Undecane[b]	0.8 – 0.95 mg/L	4.9 mg/L
Trimethylbenzene[b]	BDL	BDL

Except for Varsol™ compounds (see 2), values shown for the pervaporation product stream represent average values from April 24 to May 4, 1999.

BDL = below detection limits.

(a) An estimated value based on a pervaporation residual sample analyzed for calcium on May 25, 1999.

(b) These were the three compounds used to represent Varsol™, a petroleum distillate mixture that is a secondary contaminant at the site; ranges given for decane and undecane represent the average of 2 data points collected on April 26 and May 3, and the average of 3 data points collected on April 19, April 26, May 3, respectively.

During this project, the high calcium concentrations in the regenerated surfactant were addressed by adding fresh surfactant to the recovered surfactant in a 1:2 ratio to bring about a dilution effect, (i.e., dilution factor of 1/3 = 33% as shown in Table 5-5). This procedure also reduced contaminant concentrations to a level that was acceptable to State of North Carolina regulators for reinjection. This procedure is not generally favorable as it reduces the quantity of reusable surfactant when surfactant recoveries are high (i.e., greater than [1-dilution factor]). However if the overall surfactant recovery efficiency inclusive of both subsurface and aboveground surfactant losses is ≤ [1-dilution factor], and the site is being remediated using a panel by panel approach, the loss of reusable surfactant impacts just 1 panel of the entire remediation (see Section 6.1). Ion exchange was considered as a potentially effective means of removing the excess calcium; however due to the complexity of the surfactant stream, and the necessity of removing both calcium and chloride ions, this approach is not economically feasible. Additional technology development to improve the quality of surfactant recovered by MEUF or alternative surfactants that can avoid the calcium concentration problem while maintaining the appropriate cmc characteristics are necessary to fully realize the cost benefits of surfactant reuse.

Table 5-5. Composition of Recycled Surfactant Injected

Batch #	Volume (gal)	Contaminants (mg/L)	Surfactant (4%wt)		IPA (16%wt)	
			Recycled	Fresh	Recycled	Fresh
A1	2,760	PCE: 46.8 Decane: 3.6 Undecane: 2.7	66%	34%	2%	98%
B5	2,800	PCE: 13.7 Decane: <2.5 Undecane: 3.6	62%	38%	21%	79%
C5	2,260	PCE: 43.3 Decane: 3.1 Undecane: <2.5	67%	33%	23%	77%

Note: Tank A1 was estimated to contain 3.4wt% IPA before the addition of six drums of IPA and thorough mixing with air. The result of this mixing was a considerable loss of IPA due to volatilization before analysis and final blending. Calcium concentrations are not shown. 1,3,5-Trimethylbenzene, one of the three Varsol™ marker compounds, was below quantification limits (2.5 mg/L with 500:1 sample dilution due to surfactant) for all three samples, and is therefore not shown.

5.1.3   Post SEAR Groundwater Monitoring. Limited post-SEAR groundwater monitoring was conducted to examine the long-term effects of SEAR treatment on the aquifer. There were no regulatory compliance issues to address regarding the impact of residual chemicals remaining in the aquifer following SEAR treatment. Additionally, funding for this effort was very limited. Therefore, although the scope of the post-SEAR monitoring could have been quite extensive, it was focused primarily on determining the impact of unremoved DNAPL in the test zone. This was accomplished by monitoring select wells for reinfiltration of free-phase DNAPL from treated zones that had only been partially remediated, and by collecting groundwater samples to observe PCE concentration rebound in the test zone. It should be recognized that the post-SEAR monitoring is greatly complicated by free-phase DNAPL and aqueous plumes adjacent to the treatment zone that are migrating back into the remediated zone. (Free-phase DNAPL reentry into the treated zone is much like taking the first slice out of a fruit pie; the filling from the uncut portions of the pie flows into the void.)

The results of the post-SEAR groundwater monitoring are provided in Tables 5-6 and 5-7. Due to the acetone concentrations observed during the first post-SEAR sampling round, IPA was added as an analyte to the second round of post-SEAR groundwater monitoring conducted in February 2001. The sampling locations can be found in Figures 4.1 and 4.4 of Appendix G. Several general observations can be made: (1) PCE concentrations are slightly elevated from post-SEAR conditions; (2) PCE is being reductively dechlorinated in the aquifer, as shown by comparable concentrations of PCE and TCE, as well as significant concentrations of cis-1,2-dichloroethene, at several sampling locations; (3) IPA is degrading, as shown by the appearance of acetone. The presence of IPA, as well as surfactant, has likely stimulated reductive dechlorination at this site, as pre-SEAR groundwater sampling showed PCE to be the predominant contaminant, and only limited concentrations of TCE appearing in the test zone (compare with Table 3.5 of the DNAPL Site Characterization Report). The increase in PCE concentrations since the end of the SEAR demonstration is not surprising due to the presence of residual DNAPL in the basal silt zone that was not removed during surfactant flooding. It should be noted that PCE concentrations at MLS-2T remain below 1 mg/L, supporting the observation that residual DNAPL was effectively removed from the more permeable upper zones. The post-SEAR PCE concentration at MLS-2M for both sampling events (780 and 1,100 mg/L) is well above the aqueous solubility limit for PCE (240 mg/L); however, free-phase DNAPL has been observed as a milky white microemulsion in samples from this location; therefore these results are attributed to DNAPL that was collected into the groundwater sample. The five order of magnitude difference in PCE concentrations between MLS-2T and MLS-2M suggests that plume transport, from the DNAPL that remains in the basal silt to the overlying fine sands, is diffusion limited. The high permeability contrast that limited mass transfer of PCE under a forced gradient, high-solubilization system (SEAR) also limits mass transfer of dissolved PCE under static groundwater conditions from the low permeability zone. Thus it is expected that there is little "potential" for plume transport from this low permeability zone.

In addition to the data provided in Tables 5-6 and 5-7, VOC concentration data have been collected at Site 88 monitoring wells as part of the basewide long-term monitoring program. In Table 5-8, pre-PITT1, pre-SEAR, mid-SEAR and post-SEAR VOC data are provided at several of these Site 88 wells. The well locations can be found in Figure 3.2 of the Appendix G. The PCE concentrations fluctuate with time, but there is insufficient data to suggest trends that can be attributed directly to SEAR operations. In fact, of the monitoring wells sampled in the long-term monitoring program, only wells MW02 and MW04 are located hydraulically downgradient of the SEAR demonstration area. However, a similar variability in VOC concentrations is observed regardless of sampling location, which suggests that other factors are contributing to the variability in VOC concentrations at the long-term monitoring wells.

Table 5-6. Post-SEAR Groundwater Monitoring Results May 2000 Sampling Event

Compound	Sampling Point and Contaminant Concentration (mg/L)					
	RW01	RW02	MW10IW	MW10IWD	ML2T	ML2M
2-Butanone	1,000 U	760 J	10 U	10 U	560 J	1,000 U
1,1-Dichloroethane	500 U	500 U	5 U	5 U	500 U	400 J
Acetone	25,000	73,000	10 U	10 U	54,000	4,800
Carbon Disulfide	500 U	500 U	5 U	5 U	500 U	500 U
Cis-1,2-Dichloroethene	7,900 J	1,200	44	28	500 U	1,200
Methylene Chloride	500 U	500 U	5 U	5 U	500 U	500 U
Tetrachloroethene	43,000	89,000	290	280	2,300	780,000
Trans-1,2-Dichloroethene	500 U	500 U	5 U	5 U	500 U	500 U
Trichloroethene	690	89,000	160	170	640	1,000
Vinyl Chloride	910	750	2 U	2 U	200 U	200 U
Isopropyl Alcohol	12,000	43,000 JN	1,800 JN	80 JN	31,000	530 JN

U = not detected at reported quantitation limit
J= concentration estimated
JN = Estimated/tentative identification because no standards and calibrations were run for IPA.

Table 5-7. Post-SEAR Groundwater Monitoring Results February 2001 Sampling Event

Compound	Sampling Point and Contaminant Concentration (mg/L)					
	RW01	RW02	MW10IW	MW10IWD	ML2T	ML2M
2-Butanone	5 U	2,500 U	5 U	5 U	5 U	500 U
1,1-Dichloroethane	1	500 U	1 U	1 U	1 U	71 J
1,1-Dichloroethene	13	500	1	1 U	1 U	240
Acetone	100,000	400,000	5 U	5 U	160,000	440,000
Carbon Disulfide	0.6 J	100 U	1 U	1 U	1 U	100 U
Chlorobenzene	4.0	500 U	1 U	1 U	1 U	190
Cis-1,2-Dichloroethene	6,700 J	29,000	34	32	180 U	1,100
Ethylbenzene	11	500 U	1 U	1 U	1 U	100 U
Methylene Chloride	1 U	500 U	1 U	1 U	1 U	100 U
M,P-Xylene	44	500 U	1 U	1 U	1 U	100 U
O-Xylene	8	500 U	1 U	1 U	1 U	100 U
Tetrachloroethene	65,000	19,000	200	340	46	1,100,000
Toluene	2	500 U	1 U	1 U	1 U	100 U
Trans-1,2-Dichloroethene	37	1,000 U	2 U	2 U	3	200 U
Trichloroethene	1,500	24,000	150	170	4,700	1,500
Vinyl Chloride	960 J	2,000 J	2 U	2 U	8	200 U
Isopropyl Alcohol	50 U	5,300,000	50 U	50 U	1,200,000	44,000,000 JN

U = not detected at reported quantitation limit
J= concentration estimated
JN = Estimated/tentative identification because no standards and calibrations were run for IPA.

Free-phase DNAPL interface measurements collected during post-SEAR groundwater monitoring are compared against baseline conditions obtained prior to initiating SEAR operations in Tables 5-9 and 5-10. A comparison of the pre-SEAR and post-SEAR results show that in all wells where free-phase DNAPL was initially detected and measured (i.e., depth to DNAPL from top of well casing), that post-SEAR DNAPL levels are lower than pre-SEAR DNAPL levels. This indicates that SEAR did have a long-term impact on DNAPL levels in the aquifer. At EX05, a free-phase DNAPL interface was

not previously detected, and the post-SEAR data shows that DNAPL has been slowly accumulating in the well sump.

Table 5-8. VOC Concentration Trends at Selected Site 88 Long-Term Monitoring (LTM) Locations

Well ID	Compound				
	PCE	**TCE**	**cis-1,2-DCE**	**trans-1,2-DCE**	**VC**
MW01					
(pre- PITT1) May 15, 1997	ND	ND	ND	ND	ND
(pre-SEAR) January 21, 1999	4	ND	ND	ND	ND
(mid-SEAR) July 27, 1999	ND	ND	ND	ND	ND
(post-SEAR) January 18, 2000	ND	ND	ND	ND	ND
MW02					
(pre-PITT1) May 15, 1997	9,100	96	NA	41	ND
(pre-SEAR) January 21, 1999	3,300	160	14	ND	ND
(mid-SEAR) July 27, 1999	12,000	130	31	ND	ND
(post-SEAR) January 18, 2000	10,000	370	29	ND	ND
MW02IW					
(pre-PITT1) May 15, 1997	3,400	120	NA	12	ND
(pre-SEAR) January 21, 1999	1,100	140	44	ND	ND
(mid-SEAR) July 27, 1999	4,900	210E	64	ND	ND
(post-SEAR) January 18, 2000	7,500	270	81	ND	ND
MW04					
(pre-PITT1) May 14, 1997	ND	ND	ND	ND	ND
(pre-SEAR) January 21, 1999	6	ND	ND	ND	ND
(mid-SEAR) July 27, 1999	ND	ND	ND	ND	ND
(post-SEAR) January 18, 2000	ND	ND	ND	ND	ND
MW05					
(pre-PITT1) May 13, 1997	3,000	42	NA	38	ND
(pre-SEAR) January 21, 1999	1,300	33	10	ND	ND
(mid-SEAR) July 27, 1999	6,500	46	23	ND	ND
(post-SEAR) January 18, 2000	5,700	38	23	ND	ND
MW05IW					
(pre-SEAR) May 13, 1997	1,400	910	NA	600	ND
(pre-SEAR) January 21, 1999	910	1,500	1,100	18	ND
(mid-SEAR) July 27, 1999	3,400	2,100	1,800	24	ND
(post-SEAR) January 18, 2000	3,900	2,600	1,900	20	ND

Note: Concentrations are in μg/L.

Tables 5-9 and 5-10 also show an increase in DNAPL levels over time since the end of the SEAR demonstration; however they are still lower than pre-SEAR DNAPL levels. It is fully expected that DNAPL from beyond the treatment zone is now contributing to rising DNAPL levels in wells inside the treatment zone.

Table 5-9. Free-phase DNAPL Interface Measurements

Well ID	DNAPL level measurements (Feet Below Top of Well Casing)			
	February 1998 (pre-SEAR)	August 1999 (0 mo. post-SEAR)	May 2000 (9 mo. post-SEAR)	February 2001 (18 mo. post-SEAR)
EX01	17.1	19.45	18.82	18.40
EX02	20.2	20.97	20.70	20.63
EX04R	NM	19.52	19.22	19.18
EX05	NP	NP	21.53	21.55
IN01	19.4	NP	NP	NP
IN02	NP	NP	NP	NP
HC01	21.0	NP	NP	NP
RW01	18.6	NP	19.57	19.25
RW02	18.2	19.45	18.95	18.92
RW04	17.2	16.8	17.26	17.38
RW06	16.8	17.95	17.65	17.64

NM = not measured.
NP = no product.

Table 5-10. Changes in DNAPL Interface Elevations

Well ID	Change in DNAPL interface elevations (ft) referenced to pre-SEAR DNAPL levels		
	August 1999 (0 mo. post-SEAR)	May 2000 (9 mo. post-SEAR)	February 2001 (18 mo. post-SEAR)
EX01	-2.35	-1.72	-1.3
EX02	-0.77	-0.5	-0.43
EX04R	NA	NA	NA
EX05	NA	NA	NA
IN01	NA	NA	NA
IN02	NA	NA	NA
HC01	NA	NA	NA
RW01	NA	-0.97	-0.65
RW02	-1.25	-0.75	-0.72
RW04	0.4	-0.06	-0.18
RW06	-1.15	-0.85	-0.84

NA = not applicable.

5.2   Data Assessment

Data quality issues can be grouped into the following categories:

(1) Analytical data quality, which includes quality assurance and quality control issues (QA/QC), analytical detection limits, analytical difficulties encountered and observations of outlying data points within a data set;

(2) Sampling quality, which addresses the adequacy of sampling locations and the numbers of samples collected, as well as sampling techniques that can cause errors in the analytical results; and

(3) Data interpretation, which includes any field occurrences that influence the accuracy (and therefore interpretation) of the data collected although there is no fault with either the sampling or analytical process, and any theoretical limitations to data intepretation.

It is recognized that in some instances data quality may be influenced by more than one factor (category).

In evaluating the analytical data quality, there are some issues that are peculiar to the composition (i.e., high concentrations of PCE, IPA and surfactant), of the extracted SEAR effluent. Surfactant can foul gas chromatograph (GC) columns as well as introduce noise into the analytical results, particularly as surfactant concentrations fluctuate from sample to sample. High VOC concentrations can also be destructive to conventional analytical equipment. Generally, the analytical methods used to accommodate the presence of surfactant and high VOC concentrations tend to increase the method detection limit. The purge and trap method used by the EPA on pervaporation samples and monitoring samples requires sample dilution to minimize surfactant concentrations in the sample being injected onto the capillary or packed GC column. Independent of the problems presented by surfactant, sample dilution may also be required to normalize the VOC concentration to a range that is consistent with the calibration range of the GC. In either case inaccuracies result; for example, higher detection limits when packed columns are used for detection without sample dilution, or additional error in the analytical data introduced as a result of sample dilution. The direct injection method used by Duke Engineering and Services permits sample analysis without errors associated with dilution. However, unlike purge and trap, where the contaminant is volatilized before injection onto the column, with direct injection, contaminants are directly injected onto the column (with water and surfactant); therefore small amounts of surfactant can introduce noise into the analytical result (because of the partitioning of the contaminant into the surfactant). In addition, the use of a packed GC column for direct injection (to minimize column fouling that is associated with direct injection of capillary columns), results in higher detection limits. Using a packed column, the detection limits for PCE are between 25 and 50 mg/L, and between 500 and 1,000 mg/L for IPA. However the detection limits for IPA may be reduced to 25 mg/L or (0.0025%) when a capillary column is used. The PCE detection limit for purge and trap using a megabore capillary column was 0.05 mg/L; however with the minimum 40x dilution factor used to avoid foaming in the purge and trap, the effective PCE detection limit was not less than 2 mg/L. Some samples required higher than 40x dilution to reach the linear range of the detector and these had proportionately higher effective detection limits. In evaluating the higher PCE detection limits of SEAR-unique analytical methods, it should be recalled that the endpoint goal of SEAR remediation is source zone removal, not compliance with drinking water standards; therefore, the fact that these methods did not achieve MCLs is not significant. These analytical limitations were a minor issue. However, for groundwater samples collected to monitor dissolved PCE concentrations beyond the treatment zone (i.e., the underlying aquitard), Castle Hayne aquifer (the aquifer below the shallow aquifer being treated) and remote downgradient wells, accomplishing the lower detection limits was critical. To address this issue, samples that were not expected to contain surfactant/IPA were segregated from samples containing surfactant/IPA. Also samples expected to contain high concentrations of the target constituent were analyzed separately from samples with low concentrations. For samples containing low surfactant (<0.01 wt%), low PCE, and low IPA concentrations (<50 mg/L), an analytical detection limit of 0.05 mg/L for PCE and 25 mg/L for IPA could be achieved. There was some difficulty in quantifying Varsol™ compounds in the influent and effluent pervaporation streams due to the presence of surfactant and the need for sample dilution. This impacted performance assessment of pervaporation for Varsol™ removal,

however, because pre- and post- SEAR Varsol™ sampling was conducted as an additional regulatory requirement (see Section 7.1), this did not present a compliance issue.

For surfactant analysis, two different methods were used: hyamine titration by Duke Engineering & Services (for the analysis of both surfactant injectate-batch samples and groundwater samples collected from the extraction wells) and liquid chromatography by the University of Oklahoma for the analysis of UF samples. A consistent variance of about 10%-15% was noted between the two methods, with the liquid chromatography generally yielding higher surfactant concentrations. For consistency, the surfactant concentrations in the recovered surfactant batches (following UF) were quantified using the hyamine titration method for reconstituting the surfactant solution for reinjection. Surfactant detection limits for the LC method were not an issue. Surfactant detection limit for the hyamine titration method was a function of the available sample volume, which was an issue at the MLSs. To reach the detection limit of 0.01% (100 mg/L) required 60-70 ml of sample, which was not always available at some of the MLSs. To reach a detection limit of 0.05% (500 mg/L) required 12-14 ml of sample, which was easier to obtain, but because of the need to purge MLS points before sampling, still presented some challenges.

Another factor that impacted VOC analytical data quality at certain well locations and MLS points was the presence of free-phase DNAPL. The amount of free-phase DNAPL collected in the groundwater sample varied from sample to sample, which increased the error in the PCE concentration data for samples with free-phase DNAPL. At the bottom MLSs, which corresponded to the basal aquifer zone with significant quantities of free-phase of DNAPL, the DNAPL volume collected also minimized the aqueous fraction available in the sample for surfactant analyses.

As mentioned above, the collection of a sufficient volume of groundwater from the MLSs in order to produce a sample that could be meaningfully analyzed was limited. This was due both to the sampling equipment available during the majority of the SEAR demonstration as well as the low permeability sediments that were being sampled. This was somewhat compensated for by sampling other MLS points that could yield a sufficient volume of groundwater; therefore samples were collected from MLS-2 when difficulties were encountered with MLS-1 and MLS-4. In addition, a vacuum leak prevented collection of samples at MLS-1T during the surfactant flood; this was corrected by replacing the tubing fittings on all the MLSs in preparation for the post-SEAR PITT. During the post-SEAR PITT, a vacuum pump was used with a tubing manifold to collect samples from all six MLS locations. The vacuum pump with manifold was initially believed to be a superior method for sampling the MLSs compared to the use of a peristaltic pump (which was the sampling method used during the surfactant flood). However, because of the longer period of time and greater vacuum that had to be applied to the middle and bottom sampling points in order to fill a sample vial, the vacuum pump apparently caused vaporization (loss) of tracers from samples collected from the low permeability zone (i.e., MLS-M and MLS-B sampling points). We believe this contributed to the noisy tracer data from these sampling points in the post-SEAR PITT. For this reason, a vacuum pump is not recommended for recovering groundwater samples containing VOCs from MLSs installed in low permeability zones.

During field UF operations, there were some equipment difficulties encountered that necessitated a modification to the analytical procedure and frequent recalibration of the analytical equipment. Therefore, fewer samples were analyzed; however, both daily and longer-term mass balance calculations showed good agreement (within 4%), which indicates that the results obtained were reasonably accurate.

With respect to performance assessment, while considerable data was collected for evaluating pre- and post-SEAR DNAPL saturations, only a subset of this data was usable. The pre-SEAR PITT provided valuable baseline DNAPL conditions in the test zone, although later data suggests that, because of the permeability contrast in the basal silt layer, the initial PITT did not detect a portion of the DNAPL that was present in the bottom of the shallow aquifer. Supporting evidence of this can be seen in Figure 5-10, that shows IPA poorly penetrated the lower zone during the surfactant flood. It appears that tracer may have been hydraulically retarded in the lower permeability zone and was slowly bleeding out of it during late-time of the PITT and that some of the tail data was not captured before the PITT was terminated. Hence the lower than expected tracer recoveries, lower than expected swept pore volume, and an underestimate of the DNAPL volume in the test zone. The pre-SEAR PITT did, however, accurately detect and measure the volume of DNAPL in the accessible (i.e., higher permeability) zone above approximately 18 ft (5.5 m) bgs. Regarding the future use of PITTs, the influence of permeability heterogeneities should be carefully considered in future design.

During the post-SEAR PITT, the unexpected sorption of an impurity in the surfactant formulation caused interference with the partitioning tracers, making the post-SEAR PITT data unusable. The sorption of the surfactant impurity resulted in the false detection of DNAPL as tracers partitioned to the sorbed surfactant impurity. There are two main reasons that the interfering effects of the surfactant impurity on the post-SEAR tracers were not discovered during soil column studies. The first reason is that during the PITT tracer selection process, tracers were noted to sorb at low levels even to clean Camp Lejeune soils due to the occurrence of relatively high sedimentary organic carbon content (i.e., f_{oc} in the sediments), as documented in the pre-SEAR PITT report (Duke, 1999c). Thus, even though some tracer retardation was observed during initial soil column studies that included post-surfactant flooding tracer tests, it was misattributed to this background phenomena. Secondly, with the special effort devoted to the development of a custom surfactant to meet project objectives, funds and resources to examine effects such as surfactant impurities were very limited. Finally, it should be noted that any sorption effect observed in the laboratory was further aggravated in the field due to the lengthened residence time (12 days per pore volume) in the low permeability aquifer at Camp Lejeune.

Since the completion of the SEAR demonstration, several studies have been conducted to elucidate the post-SEAR PITT sorption issue. The surfactant manufacturer, formerly Condea Vista, now Sasol, has shown that by modifying the Alfoterra 145-4PO sulfate™ surfactant synthesis process with the use of a proprietary catalyst, that false tracer partitioning to the sorbed surfactant impurity can be completely avoided when sodium is used as the electrolyte. On the other hand, soil column studies conducted at The University of Texas at Austin using surfactant synthesized by the alternate method indicate that when calcium is used instead of sodium as the electrolyte, that extended post-surfactant water flooding is required to avoid tracer sorption. This suggests the possible formation of surfactant-calcium complexes that subsequently sorb to the aquifer solids. Because the low permeability, high clay conditions at Camp Lejeune require calcium as an electrolyte to prevent the mobilization of soil fines, and extended water flooding will increase project costs, surfactants other than the Alfoterra should be considered under these subsurface conditions if a post-SEAR PITT is desired. One such alternative that has been used at other chlorinated solvent DNAPL sites is the Aerosol MA-80I surfactant produced by Cytec, although this surfactant did not meet the secondary requirement of this project for a low critical micelle concentration (cmc) surfactant that can be recycled by ultrafiltration.

Due to difficulties encountered with the accurate interpretation of the post-PITT data, SEAR performance was ultimately evaluated by using the pre-SEAR PITT results along with the pre- and post-SEAR soil sampling data. Note that the pre-SEAR soil samples were not used to generate an initial DNAPL volume estimate because the pre-SEAR soil sampling events were designed to locate DNAPL

and to roughly delineate the boundaries of the DNAPL zone, but the data set was not suitable for estimating DNAPL volume. Rather pre-and post-SEAR soil samples were compared to examine trends in removal of DNAPL with depth and from certain locations within the test zone.

Analysis of the post-SEAR soil core data indicates that approximately 5.2 ± 1.6 gals of DNAPL remain in the zone that was effectively swept by the tracers and surfactant (i.e., the zone above approximately 17.8 ft bgs). In addition, data analysis from the post-SEAR soil cores indicates that approximately 23.5 ± 5.5 gals remain in the mid-to-bottom zone that was not effectively penetrated by the tracers or surfactant (i.e., from 17.8 ft bgs down to the clay aquitard). The initial PITT estimated that the volume of DNAPL in the test zone before the surfactant flood was approximately 81 ± 7 gals (74 to 88 gals). It is concluded here that the total volume of DNAPL present in the test zone before the surfactant flood is best represented by both the volume of DNAPL measured by the pre-SEAR PITT plus the volume of DNAPL estimated (from soil core data analysis) for the zone below 17.8 ft bgs, for a total pre-SEAR DNAPL volume of approximately 105 gals.

With DNAPL effectively removed from the higher permeability upper zone (i.e., above 17.8 ft bgs), plume formation in now restricted to the DNAPL that remains in the basal silt zone. Given the hydrogeologic conditions at Site 88, there is little "potential" for plume transport from the basal silt into the overlying groundwater transport zone because: (a) static hydraulic gradients are vertically downward throughout the surficial aquifer [i.e., static water levels are several feet higher in the the surficial aquifer than in the underlying confined aquifer]; and (b) the density gradient for dissolved PCE in the basal silt is also downward. Therefore, the remaining PCE in the basal silt is essentially immobilized by the combination of downward hydraulic gradients and the presence of the thick underlying clay layer. This leaves diffusion as the primary transport mechanism for the mass flux of PCE from the basal silt to the overlying groundwater advection zone. This is consistent with the five orders of magnitude difference in PCE concentrations between MLS-2T (17 ft bgs) and MLS-2M (18.5 ft bgs), as observed in the post-SEAR monitoring results (see Section 5.1.3).

As discussed above, the post-SEAR soil core data analysis subdivided the post-SEAR DNAPL volume into two depth intervals: the zone above 17.8 ft bgs (i.e. the zone swept by the initial PITT); and the zone below 17.8 ft bgs (the zone not effectively swept by the initial PITT). From this, it can be inferred that the surfactant flood recovered between 92% to 96% of the DNAPL that was present in the pore volume that was swept by the pre-SEAR PITT (i.e. above 17.8 ft bgs). Hence, summing the two zones as a basis for the total pre-SEAR volume of DNAPL, the surfactant flood recovered approximately 72% of the DNAPL from the entire SEAR demonstration test zone, which includes all zones above the aquitard. For more complete details regarding performance assessment of the SEAR demonstration, see Section 9 of the SEAR Final Report (DE&S, 2000).

A sensitivity analysis was conducted on the post-SEAR soil sampling data to estimate the minimum number of soil samples that were required to derive an accurate DNAPL volume estimate. These results, presented in Appendix F, show that the set of 60 soil samples provided an acceptable dataset for performance evaluation of a small site such as Site 88. The accuracy of the any final DNAPL volume estimate by soil cores also assumes the following:
- The samples represent average values for that part of the subsurface that they are chosen to represent. That is, the samples meet the requirement that they constitute NAPL concentration measurements for the representative elementary volume of that part of the aquifer.

- The method for recovery and handling of the soil core did not result in the loss of significant amounts of NAPL.

- The soil samples were recovered from all parts of the NAPL zone under remediation, in particular, parts of the geosystem that have relatively high and relatively low permeabilities.

Note that these issues were addressed at Camp Lejeune by collecting samples from 12 locations, by recovering continuous soil cores over as much of the treated aquifer thickness at each location as possible, by subdividing these large cores into 6 inch core samples for analysis, and by using plastic soil core liners and in-field methanol preservation of soil samples to avoid volatilization of DNAPL. Also shown in Appendix F is the effect of reducing the overall number of sampling locations as well as uncertainties in other sampling variables on the accuracy of the DNAPL saturation estimate. Note that at many sites with similar dimensions to Lejeune, it is typical to collect no more than 20 soil samples, which could be equated to reducing the number of soil sampling locations to 4 from 12, if the vertical sampling frequency is kept the same. Under these circumstances, for this particular data set, the coefficient of variation increases from 0.06 to 0.3 and the % error in the DNAPL saturation estimate changes from 29% to 41% with all other variables kept constant. That a greater error does not result with such a drastic reduction in samples collected is because of the high intrinsic error associated with using soil samples to calculate the DNAPL volume under low DNAPL saturation conditions.

5.3   Technology Comparison

A comparison of the surfactant flooding technology to selected alternative DNAPL removal technologies is provided in Table 5-11. It should be remarked that there is no single DNAPL removal technology that can be used at every site, and that technology selection should always be made on a site-specific basis. Furthermore, the need for sufficient source zone characterization, and the difficulty of adequately characterizing a hetereogeneous zone (such as a basal silt layer), will affect the design, cost and performance all remedial technologies.

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Table 5-11. Advantages and Disadvantages of Selected DNAPL Removal Technologies

	Steam Flooding	Surfactant/Cosolvent Flooding	Six Phase Heating	In-Situ Chemical Oxidation
Applicability	Applicable to NAPLs, especially beneficial for viscous oils, coal tars	Applicable to NAPLs	Applicable to NAPLs	Applicable to dissolved contaminants, effectiveness has not been demonstrated for NAPLs
Laboratory Design	Minimal laboratory development	Extensive laboratory testing to optimize process	Minimal laboratory development	Some laboratory testing
Field Design	Requires detailed site characterization: 1. Locate the source zone and delineate its extent; 2. Map the hydrostratigraphy; 3. Measure basic aquifer and soil Parameters. 4. Characterize the capillary barrier (aquitard) relative to NAPL mobilization design. Simulations needed for field design and implementation	Requires detailed site characterization: 5. Locate the source zone and delineate its extent; 6. Map the hydrostratigraphy; 7. Measure basic aquifer and soil parameters 8. Characterize the capillary barrier (aquitard) relative to NAPL mobilization design Simulations needed for field design and implementation	Requires detailed site characterization: 1. Locate the source zone and delineate its extent; 2. Map the hydrostratigraphy; 3. Measure basic aquifer and soil parameters. 4. Characterize the capillary barrier (aquitard) relative to NAPL mobilization design. Simulations helpful for improved field design and implementation	Requires detailed site characterization: 1. Locate the source zone and delineate its extent; 2. Map the hydrostratigraphy; 3. Measure basic aquifer and soil parameters. Simulations for field design and implementation i.e. quantifying the location and volume of NAPL
Hydrogeologic constraints	Poor sweep caused by channeling and preferential flow of steam, not amenable to means of mobility control	Mobility control such as polymer flooding or surfactant-foam flooding is recommended to address the issue of effective sweep through heterogeneous zones, providing that aquifer permeability and thickness is sufficient	Performance is best in relatively low permeability zones; in high permeability zones, too much water will have to be vaporized for contaminant removal	Not amenable to mobility control and hence will be constrained by permeability variations

Table 5-11. Advantages and Disadvantages of Selected DNAPL Removal Technologies (Continued)

	Steam Flooding	Surfactant/Cosolvent Flooding	Six Phase Heating	In-Situ Chemical Oxidation
Effect on subsurface	Significant quantities of NAPL can be removed. Thorough measurements of final NAPL saturations in treated soils is lacking. The long-term effect of aquifer heating is unknown, although when implemented in carbonate aquifers, heat induced precipitation of calcium carbonate can reduce aquifer permeability and potentially affect vapor recovery.	Use of appropriate biodegradable surfactant/cosolvent mixtures reduce NAPL saturations to less than 0.05%	Significant quantities of NAPL can be removed. Thorough measurements of final NAPL saturations in treated soils is lacking. The long term effect of aquifer heating is unknown, although when implemented in carbonate aquifers, heat induced precipitation of calcium carbonate can reduce aquifer permeability and potentially affect vapor recovery.	NAPLs destroyed in-situ in the aqueous phase. Has the potential to oxidize naturally occurring organics in the aquifer, thereby increasing the total mass of oxidant required to treat the target contaminants.
NAPL mobilization	Can mobilize or recondense NAPL to unheated regions, e.g., outside the test area, and hence requires extensive design and monitoring	With proper hydraulic control and neutral buoyancy surfactant flooding, potential for NAPL mobilization will be minimized	NAPL mobilization is generally not a cause for concern	NAPL mobilization is generally not a cause for concern
Performance assessment	Change in NAPL composition (fractionation) can affect performance assessment by tracer tests	Well-designed surfactants do not change NAPL composition; surfactant sorption can affect performance assessment by tracer tests, however this is preventable in the design process	Change in NAPL composition can affect performance assessment by tracer tests	Limited by dissolution rate of NAPL; change in NAPL composition can affect performance assessment

Section 6.0: COST ASSESSMENT

6.1   Cost Performance

This section provides full-scale cost estimates for SEAR application at a site with similar conditions to Camp Lejeune assuming similar performance to the ESTCP demonstration. A summary of Camp Lejeune site conditions is provided in Table 3-1. Although most system specifications used in the full-scale estimates are identical to what was employed in the Camp Lejeune demonstration, several modifications have been made to avail of recent technology advancements. For example, significant progress has been made in the development of customized surfactants since the Camp Lejeune demonstration, including the improved tailoring of surfactants to PCE. Surfactants such as the Alfoterra 123-8PO sulfate™ have been used in the field for Navy special fuel oil (NSFO) and coal tar removal, and show improved microemulsion viscosity compared to Alfoterra 145-4PO sulfate™ which was used at Camp Lejeune. Both of the named contaminants are highly viscous, for example, the viscosity of NFSO at 61 °C is 150 centipoise (cp), while the viscosity of coal tar at 38 °C is 32 cp, in comparison to PCE which has a viscosity of 0.9 cp at at 25 °C. Yet, the cosolvent requirement for the NFSO and coal tar floods did not exceed 8 wt% IPA. This is a 50% reduction in IPA content, as compared to the 16 wt% IPA requirement for PCE using Alfoterra 145-4PO sulfate™. A new surfactant, the Alfoterra I12-3PO sulfate™, has been especially tailored for PCE and displays much improved phase behavior and viscosity in comparison to the Alfoterra 145-4PO sulfate™ due to the uniformity of and decreased carbon length of the surfactant tail.[2] For this reason the full-scale SEAR estimates assume the use of Alfoterra I12-3PO sulfate™ and no more than 8 wt% IPA. It is possible that as little as 4 wt% IPA could be used; however, this requires additional laboratory testing with the Camp Lejeune DNAPL and soils.

Another innovation that has been included in the SEAR full-scale estimates is the use of chemical metering pumps and in-line mixing for surfactant injectate preparation. This avoids manual chemical measurements for improved accuracy of the surfactant composition and reduced labor costs, and minimizes the required tankage capacity for reduced construction costs when the remediation is sufficiently large. Additionally, an on-line gas chromatograph (GC) has been added for the analysis of organic contaminants. This is a GC, which has been customized with a stream selector and sampling ports such that fluids from extraction wells and other monitoring points can be directly injected onto the GC column. Surfactant injectate can also be directly plumbed into an on-line GC for the analysis of cosolvent concentrations (or contaminant concentrations in the case of recycled surfactant). Surfactant fouling of the packed GC column is avoided through the use of a GC pre-column that is periodically replaced. These can be purchased for certain GC models or can be "hand-made" using stainless steel tubing filled with deactivated glass. The use of an on-line GC not only significantly reduces analytical costs, but also reduces the error involved in sample collection and transport. Finally, where applicable, mobility control measures were incorporated into the SEAR design; this is discussed further below.

Because technology application costs vary with scale, and the DNAPL source area at Site 88 is fairly small, two additional full-scale cost estimates were developed to account for larger DNAPL source areas that may be present at other sites. In addition, because surfactant-flooding costs are sensitive to the permeability (k) of the contaminated aquifer, parallel full-scale cost estimates were developed for a high permeability site with all similar characteristics to Camp Lejeune with the exception of the permeability being two orders of magnitude higher (K = 0.05 to 0.005 cm/sec). The first scale of

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[2] The I12 refers to a single tail length with 12 carbons, whereas 145 refers to a tail length that is a mixture of 14 and 15 carbons.

application chosen is that which would remediate the entire DNAPL source zone at Site 88 (including the zone already treated during the ESTCP demonstration). This is equivalent to an area of approximately 2,500 square feet for the low permeability scenario and an area of approximately 3,333 square feet for the high permeability scenario. The 32% larger treatment area for the higher permeability scenario comes from adopting a well configuration design that uses fewer wells with a greater interwell distance between injection and extraction wells, as shown in Table 6-1. This significantly reduces the number of wells, pumps, extraction well sampling locations, and the costs associated with each of these items. Another important design feature is that the high k SEAR employs polymer for mobility control, which mitigates the strong permeability contrast of the aquifer to considerably shorten the length of SEAR treatment. The addition of approximately 500 mg/L xanthan gum polymer to the surfactant formulation to form an injectate of increased viscosity is the typical use of polymer for mobility control and was the design basis for the high k mobility control floods. This option is not available for the low k SEAR design at a site like Site 88 because of the limited range of available hydraulic gradients to drive the increased viscosity polymer fluid through the low k formation. A comparison of the required flooding durations, in units of pore volumes and total number of days, for a low permeability SEAR, high permeability SEAR and high permeability SEAR with mobility control is shown in Table 6-2. It is evident that the use of polymer significantly decreases the total number of pore volumes required for the surfactant flooding and final water flooding phases, but also slightly lengthens the time required to propagate a pore volume of fluid, due to the higher viscosity of the polymer solution that is used in all phases of the SEAR test.

Table 6-1. Comparison of Well Requirements for Full-Scale SEAR Application under Low Permeability (Low k) or High Permeability (High k) Conditions at a Site Similar to Site 88, MCB Camp Lejeune, NC

	Number of injection wells (I)	Number of extraction wells (E)	Number of hydraulic control wells	Well Spacing (I-E/I-I =E-E)[a]
Low k	14	24	8	15 ft/10 ft
High k	3	6	2	55 ft/15 ft

(a) I-E refers to the interwell distance between the **i**njection and **e**xtraction points, while I-I and E-E refer to the interwell distance between the neighboring injection (**i**njection-**i**njection) or extraction (**e**xtraction-**e**xtraction) wells. In a line drive well configuration, the I-I and E-E distances are equivalent.

Using either the 2,500 or 3,333 square feet as the basic remediation unit or panel, scaled up cost estimates were obtained for a hypothetical cleanup of a 0.5 and 1.0 acre DNAPL source zone. The low permeability full-scale cost estimates, are presented in Table 6-3. The high permeability full-scale cost estimates which include mobility control are presented in Table 6-4. In developing the cost estimates, the use of PITTs for DNAPL source zone characterization and performance assessment was considered optional; thus, these costs are not included in any of the full-scale scenarios. The costs reflect conventional wastewater treatment by gravity separation, then air stripping followed by biological treatment of the unstripped organic contaminants (surfactant/IPA) and off-gas treatment of the VOCs. These costs are conservative as they assume that there is no on-site facility available for wastewater treatment, and because many states do not regulate emissions from air-strippers. Inorganic salts are assumed to be within the total dissolved solids limits for disposal. It was assumed that polymer used in the high k mobility controlled floods would have minimal impact on effluent treatment operations. For a site with wastewater treatment facilities, the conventional wastewater treatment costs reflected in

Table 6-2. Comparison of Flooding Durations for Full-Scale SEAR Application under Low Permeability or High Permeability Conditions at a Site Similar to Site 88, MCB Camp Lejeune, NC

	Initial Water Flood Duration (PV/Total Days)	Surfactant Flood Duration (PV/Total Days)	Final Water Flood Duration (PV/Total Days)	Total SEAR Duration (Total Days)
Low k	1 PV (7 days)	5 PV (58 days)	8 PV (62 days)	127 days
High k	1 PV (3 days)	5 PV (15 days)	8 PV (24 days)	42 days
High k w/mobility control[a]	1 PV (4 days)	2 PV (8 days)	3 PV(12 days)	24 days

(a) The high k mobility control design assumes equivalent if not superior performance to the high k system that does not use mobility control.

WBS Elements 4.26.30, 4.26.04, 4.34.05, 4.34.12 and 4.22.09 may be reduced or eliminated. Because the proposed remediation scheme involves SEAR treatment of a single panel at a time, it may be observed that the capital equipment costs for the wastewater treatment system do not increase with scale.

There is a significant decrease in SEAR costs when conducted at the 0.5 and 1.0 acre scales. The cost of the 1 panel "unit" is reduced by almost 50% for the low k system when implementing at the 0.5 and 1.0 acre scales. Similarly, the high k system unit cost is reduced by almost 60% for an 0.5 acre application and by >60% for a 1.0 acre application. The primary cost savings are due to the fixed design, construction and analytical costs with scale-up. Another cost benefit is the decrease in unit surfactant costs by 33% at the 0.5 and 1.0 acre scales because of the greater quantities purchased. Furthermore, it can be observed that there is a relative decrease in performance assessment costs at the 0.5 and 1.0 acre scales; this results from the assumption that it would be infeasible to engage in the same magnitude of intensive soil sampling at these scales for statistically accurate performance assessment. Still, the number of performance assessment borings selected at these larger scales, i.e., 160 and 320 borings for the 0.5 and 1.0 acre cost estimates respectively, is probably ample by comparison to standard industry practices.

Permeability also has a considerable impact on the SEAR cost. The low k full-scale SEAR costs range from approximately 150% to 290% higher than the high k full-scale SEAR costs depending on the scale of application. This is primarily reflected by higher costs in the following categories: CITT/free-phase recovery (pre-construction), well and pump installation (construction), labor (O&M), and chemicals (O&M). The higher pre-construction costs and SEAR labor costs are due to the extended flooding durations required of working in a shallow low permeability system. The higher construction costs can be attributed to the significant well and pump requirements for the low k SEAR relative to the high k SEAR (Table 6-1). The higher chemical costs are due to the high permeability contrast and limitations to applying mobility control measures at this site. The chemical cost savings with mobility control can be estimated by comparing the chemical costs of the low k SEAR application (without mobility control) to the chemical costs of the high k SEAR application (with mobility control) at all scales. This reveals a 45% reduction in chemical costs at the 1 panel scale and a 58% reduction in chemical costs at the 0.5 and 1.0 acre scales. Additionally, although the associated cost savings are not obtainable from the information provided in Tables 6-3 and 6-4, Table 6-2 shows that under high k

Table 6-3. Projected Cost of a Full-Scale SEAR System for a Site Similar to Site 88, MCB Camp Lejeune

WBS Element	Item	Item Cost ($) for 2500 sq. ft. (1 panel)	Item Cost ($) for 0.5 acre (8 panels)	Item Cost ($) for 1.0 acre (16 panels)
Preconstruction Cost				
4.07, 4.08, and 4.09	DNAPL source zone characterization	47,400	155,500	277,600
4.04	Surfactant selection	25,000	25,000	25,000
4.04	Bench-scale treatment equipment testing	25,000	25,000	25,000
4.04	Preliminary field testing[a]	51,100	50,000	50,000
4.04	CITT/free-phase recovery	79,800	638,700	1,277,400
4.04	Engineering design and modeling	69,200	263,000	380,600
	Subtotal	*297,500*	*1,157,200*	*2,035,600*
Construction Cost				
4.05	Site preparation	18,500	18,500	18,500
4.26.30	DNAPL decanting tank system installation	10,400	10,400	10,400
4.26.04	Air stripping system	57,500	57,500	57,500
4.34.05 and 4.34.12	Off-gas treatment system	89,700	89,700	89,700
4.22.09	Air stripper bottoms biotreatment system	72,600	72,600	72,600
4.23.05	Well and pump installation	168,700	1,349,700	2,699,400
4.23.05	Aboveground piping installation	49,200	49,200	49,200
4.23.05	Chemical addition system installation	20,600	20,600	20,600
4.33	Disposal of drill cuttings	1,900	15,400	30,700
4.05	Site restoration	3,000	23,800	47,500
	Indirect Capital[b]	147,600	512,200	928,900
	Subtotal	*639,700*	*2,219,600*	*4,025,000*
Operations and Maintenance Cost				
5.23.05	Chemical cost	245,300	1,401,700	2,803,300
5.23.05	Labor cost	169,500	1,355,600	2,711,200
5.07, 5.08, and 5.09	Analysis cost	71,200	328,400	622,300
5.23.05	Utilities/miscellaneous cost	16,100	128,600	257,200
	Subtotal	*502,100*	*3,214,300*	*6,394,000*
Performance Assessment Cost				
	Performance assessment	*103,700*	*177,300*	*324,700*
Full-Scale SEAR System Total Cost		1,543,000	6,768,400	12,779,300

(a) This assumes that no previous pilot-testing of SEAR, such as the completed ESTCP demonstration, has been conducted at the site.

(b) Field supervision, quality assurance, health and safety support, overhead and administrative, and contingency.

Table 6-4. Projected Cost of a Full-Scale SEAR System for a High Permeability Site With All Other Parameters Similar to Site 88, MCB Camp Lejeune

WBS Element	Item	Item Cost ($) for 3333 sq. ft. (1 panel)	Item Cost ($) for 0.5 acre (6 panels)	Item Cost ($) for 1.0 acre (12 panels)
Preconstruction Cost				
4.07, 4.08, and 4.09	DNAPL source zone characterization	47,400	155,500	277,600
4.04	Surfactant selection	25,000	25,000	25,000
4.04	Bench-scale treatment equipment testing	25,000	25,000	25,000
4.04	Preliminary field testing [a,c]	42,000	40,900	40,900
4.04	CITT/free-phase recovery	28,800	173,000	346,000
4.04	Engineering design and modeling	69,200	207,600	297,600
	Subtotal	*237,400*	*627,000*	*1,012,100*
Construction Cost				
4.05	Site preparation	18,500	18,500	18,500
4.26.30	DNAPL decanting tank system installation	10,400	10,400	10,400
4.26.04	Air stripping system	67,900	67,900	67,900
4.34.05 and 4.34.12	Off-gas treatment system	89,700	89,700	89,700
4.22.09	Air stripper bottoms biotreatment system	97,100	97,100	97,100
4.23.05	Well and pump installation	50,400	302,600	605,100
4.23.05	Aboveground piping installation	22,400	22,400	22,400
4.23.05	Chemical addition system installation	20,600	20,600	20,600
4.33	Disposal of drill cuttings	700	4,100	8,300
4.05	Site restoration	800	4,600	9,200
	Indirect capital cost[b]	113,600	191,400	284,800
	Subtotal	*492,100*	*829,300*	*1,234,000*
Operations and Maintenance Cost[c]				
5.23.05	Chemical cost	135,700	589,900	1,179,800
5.23.05	Labor cost	31,800	190,600	381,200
5.07, 5.08, and 5.09	Analysis cost	30,800	110,200	188,900
5.23.05	Utilities/miscellaneous cost	11,200	67,400	134,800
	Subtotal	*209,500*	*958,100*	*1,884,700*
Performance Assessment Cost				
	Performance assessment	*103,700*	*177,300*	*324,700*
Full-Scale SEAR System Total Cost		1,042,700	2,591,700	4,455,500

(a) This assumes that no previous pilot-testing of SEAR, such as the completed ESTCP demonstration, has been conducted at the site.
(b) Field supervision, quality assurance, health and safety support, overhead and administrative, and contingency.
(c) These costs assume the use of polymer for mobility control.

conditions, the use of mobility control cuts the required field time by almost 50%. Due to these economic benefits, and the necessity of addressing the negative influence of heterogeneities on SEAR performance, it is recommended that mobility control be incorporated into future SEAR designs.

Surfactant recovery treatment estimates were separately developed to evaluate any cost savings associated with material reuse. The basic premise of the surfactant recovery design is that for remediations larger than 1 panel, the recovered surfactant for the remediation of a given panel will be applied to the injection of the next (with the exception of the last panel). For a single panel remediation, surfactant that is recovered is reinjected as part of the overall surfactant requirement for that panel as done at Camp Lejeune. Once again, it was assumed that there are no existing on-site wastewater treatment facilities available to handle any primary or secondary waste streams produced during SEAR operations. Therefore the design of the surfactant recovery treatment system presented herein includes a conventional wastewater treatment system for processing secondary waste streams generated during surfactant recovery operations. The only difference is that the air-stripper off-gas treatment system from a conventional system is no longer necessary when surfactant recovery equipment is added.

Criteria used in developing the surfactant recovery cost estimates are provided in Table 6-5. In designing the surfactant recovery system, lease costs were assumed for remediations lasting 6 months or less, while newly purchased equipment costs were assumed for longer-term remediations. Three options were evaluated for separating contaminant from surfactant: 1) air stripping without antifoam addition (with off-gas treatment), 2) liquid-liquid extraction by a macroporous polymer process commercially available from Akzo Nobel, and 3) pervaporation. Both air stripping without antifoam addition and the macroporous polymer extraction (MPPE) system have been field tested by Surbec-Art Environmental for decontaminating SEAR waste streams during a surfactant flooding operation; therefore, the assistance of Surbec-Art Environmental was retained for generating the costs for applying these processes. Separate estimates for the MPPE system were obtained directly from Akzo Nobel. Of the three contaminant removal options, MPPE is probably the most robust alternative as it can be applied to most hydrophobic contaminants, both volatile and non-volatile, while both air stripping and pervaporation are limited to removing volatile contaminants. Although air stripping without antifoam addition has been included as a contaminant removal alternative in this cost analysis, it should be noted that great care must be taken in designing and operating such a system. Improper design and operation of an air-stripper without antifoam addition for treatment of surfactant solutions can easily lead to flooding of the column with foam. Even if foaming is avoided, contaminant removal efficiency will be greatly reduced due to the attraction of the contaminant for the surfactant micelles. Although antifoam addition would greatly reduce the tendency to foam, such additives would likely make reinjection of the subsequently recovered surfactant impossible for technical and/or regulatory reasons. For the low k scenarios, air stripping and MPPE had similar costs, and pervaporation costs were slightly higher; air stripping costs were used. For the high k scenarios, the MPPE system was the most cost-effective alternative and these costs were used.

Micellar-Enhanced Ultrafiltration (MEUF) was the only process examined for concentrating the surfactant following contaminant removal. Unlike the Camp Lejeune demonstration, which used a multiple-pass operation of MEUF to accomplish the target surfactant concentrations, the MEUF system was designed for single pass operation to minimize capital costs. This will require greater adjustments to operating parameters than a multiple-pass system that is less sensitive to changes in the influent surfactant concentrations. It was assumed that super-concentration of calcium would be addressed by adding fresh surfactant. For a 1 panel remediation, it is assumed that 30% of the total surfactant requirements will be supplied by recycled surfactant and the rest will be supplied by fresh surfactant; this allows for a >1/3 dilution factor for the recycled surfactant to adjust calcium concentrations. For a

Table 6-5. Criteria Used to Develop Surfactant Recovery Costs

Criteria	Low k	High k
Surfactant Injected	4 wt%(active) Alfoterra I12-3PO sulfate™	4 wt% (active) Alfoterra I12-3PO sulfate™
Cosolvent Injected	8 wt% IPA	8 wt% IPA
Design flowrate	6 gpm	18 gpm
Contaminant Removal Process	Air stripping	MPPE
Efficiency of Contaminant Removal Process[a]	99%	99%
Subsurface surfactant recovery	80%	80%
Average concentration of surfactant in the SEAR effluent[b]	1 wt%	1 wt%
Efficiency of surfactant recovery by MEUF	75%	75%
Days of Operation	1 panel: 127 days 0.5 acre: 889 days 1.0 acre:1905 days	1 panel: 24 days 0.5 acre:120 days 1.0 acre: 264 days
Days of Surfactant Recovery	1 panel: 58 days 0.5 acre:406 days 1.0 acre:870 days	1 panel: 8 days 0.5 acre: 40 days 1.0 acre: 88 days
Surfactant cost	$4.50/active lb for 1 panel $3.00/active lb for 0.5 and 1 acres	Same as low k
Salvage factor for capital equipment	50%	50%
Tankage requirement (c)	1 panel: 2-21,000 gallon steel tanks 0.5 or 1 acre: 7-12,000 gallon plastic tanks	1 panel: 1-21,000 gallon steel tank 0.5 or 1 acre: 2-21,000 gallon steel tanks
Analytical requirement (d)	1 panel: 30 surfactant analyses 25 calcium analyses 0.5 or 1 acre (n-1) panels: 55 surfactant analyses (includes 5 quick turnaround analyses) 50 calcium analyses	1 panel: 15 surfactant analyses 12 calcium analyses 0.5 or 1 acre (n-1) panels: 28 surfactant analyses (includes 3 quick turnaround analyses) 25 calcium analyses
Labor requirement	5 man-hrs per panel	Same as low k

(a) A 99% contaminant removal requirement accomplishes 95% contaminant removal prior to surfactant reinjection, assuming that the 1% contaminant remaining is concentrated by a factor of 5 during MEUF treatment.

(b) This value is calculated as follows. The rate of extraction is 3 times the injection rate so that the maximum surfactant concentration at the extraction wells is 1/3 of the injection concentration or (4/3)= 1.33 wt%. Then, assuming 20% surfactant loss in the subsurface, the concentration of surfactant arriving at the extraction well is 1 wt%.

(c) Each 21,000 gallon tank requires 2 recirculation pumps, and each 12,000 gallon tank requires 1 recirculation pump (but due to the slow rate of injection for the low k SEAR no more than 3 pumps are needed in operation at one time, so only 3 are purchased).

(d) Pre amendment analyses are needed for each surfactant component and post amendment analyses are required for the contaminant. The on-line GC system can address PCE and IPA analyses, therefore there is no additional costs for these components. Analytical costs for the 1 panel scale remediation or the final panel of a multiple scale remediation are twice as expensive due to the quick turnaround needed on analytical results, but only ½ as many analyses are required due to the smaller quantity of recycled surfactant being reinjected. Some quick turnaround samples have also been included for monitoring surfactant concentrations during MEUF operations.

multiple panel remediation, with the exception of the final panel, it was assumed that all of the surfactant recovered from the preceding panel, or 60% of the total surfactant injected, would be applied to the remediation of that panel. For the final panel of a multiple panel remediation, there is no reuse value of recovered surfactant due to the need to dilute recycled surfactant with fresh surfactant, and therefore, no surfactant recovery is needed. Surfactant recovery operations require additional tankage to store recycled surfactant, additional laboratory analyses to measure surfactant, cosolvent, contaminant and electrolyte concentrations before reconstitution of the surfactant formulation with fresh surfactant and other makeup chemicals (since only surfactant is recovered in the process). This has a greater impact on the low k surfactant recovery costs due to the higher surfactant requirements leading to higher volumes of surfactant being recovered. Finally, there is additional labor required to handle the recycled surfactant batches and to collect analytical samples, as well as to determine the appropriate adjustments of chemicals necessary to amend the recycled surfactant solution.

The conceptual diagram of a full-scale SEAR remediation with surfactant recovery is provided in Figure 6-1. Surfactant recovery system costs and savings are presented in Table 6-6. The surfactant recovery cost savings for the 1 panel scale high k SEAR represents 3% of the total project cost. At the 0.5 acre scale for the high k scenario, due to the higher lease costs relative to the value of recovered surfactant, the higher analytical costs and the higher tankage and pump costs, the surfactant recovery cost savings decreases to 1.3% of the total project cost. At the 1.0 acre scale, the high k surfactant recovery cost savings is equivalent to 3.3% of the total project cost. Comparable savings were not obtained at the 1 panel scale for the low k system due to equivalent lease costs for a 6 gpm and 18 gpm surfactant recovery system and the considerably longer effluent treatment duration. In fact, for the low k SEAR, surfactant recovery only shows a cost benefit at the 1 acre scale, where the cost savings represents 1.5% of the total project cost. Therefore, the longer field durations associated with the low k SEAR influences not only the subsurface treatment costs, but also surfactant recovery costs. For either the low k or high k conditions, it can also be seen that if air-stripper off-gas treatment is not required at a remediation site, that the cost benefits of surfactant recovery are significantly reduced because the credited cost shown in Table 6-6 is no longer applicable. Because the economics of surfactant recycle is a function of many site-specific variables, as well as the SEAR design, the potential benefits of surfactant recovery processes for future SEAR projects should be evaluated on a site-by-site basis.

More detailed information regarding the costs associated the application of SEAR over a single panel area, at both a low and a high permeability site is provided in Appendix H. More in-depth discussion of the full-scale SEAR design and surfactant recovery concepts, as well as presentation of PITT costs, is provided in the ESTCP Cost & Performance Report (Battelle/DE&S, 2001).

6.2   Cost Comparisons to Conventional and Other Technologies

In this section, the cost of SEAR treatment for DNAPL removal is compared to the cost of pump and treat (P&T) for DNAPL source zone containment, as well as two in-situ thermal remediation methods for DNAPL removal: steam injection and resistive heating. The pump and treat estimate was developed by Battelle, Columbus, OH. Battelle also assisted in contacting the thermal treatment vendors and obtaining budget cost estimates for full-scale application of their technologies for cleanup of the entire DNAPL source zone, (including the ESTCP demonstration area) at Site 88, MCB Camp Lejeune. The site parameters are summarized in Table 6-4. The basis of all cost estimates is the remaining DNAPL source zone at Site 88, which covers approximately 2,500 square feet. The steam injection cost estimate was based on application of steam-enhanced extraction/hydrous pyrolysis oxidation (SEE/HPO™) by Integrated Water Resources (IWR), Inc., (Parkinson, 2000). Steam injection mobilizes DNAPL toward extraction wells by injecting steam to thermally reduce surface tension. In the hydrous pyrolysis variation, air is injected along with the steam to break down chlorinated volatile organic
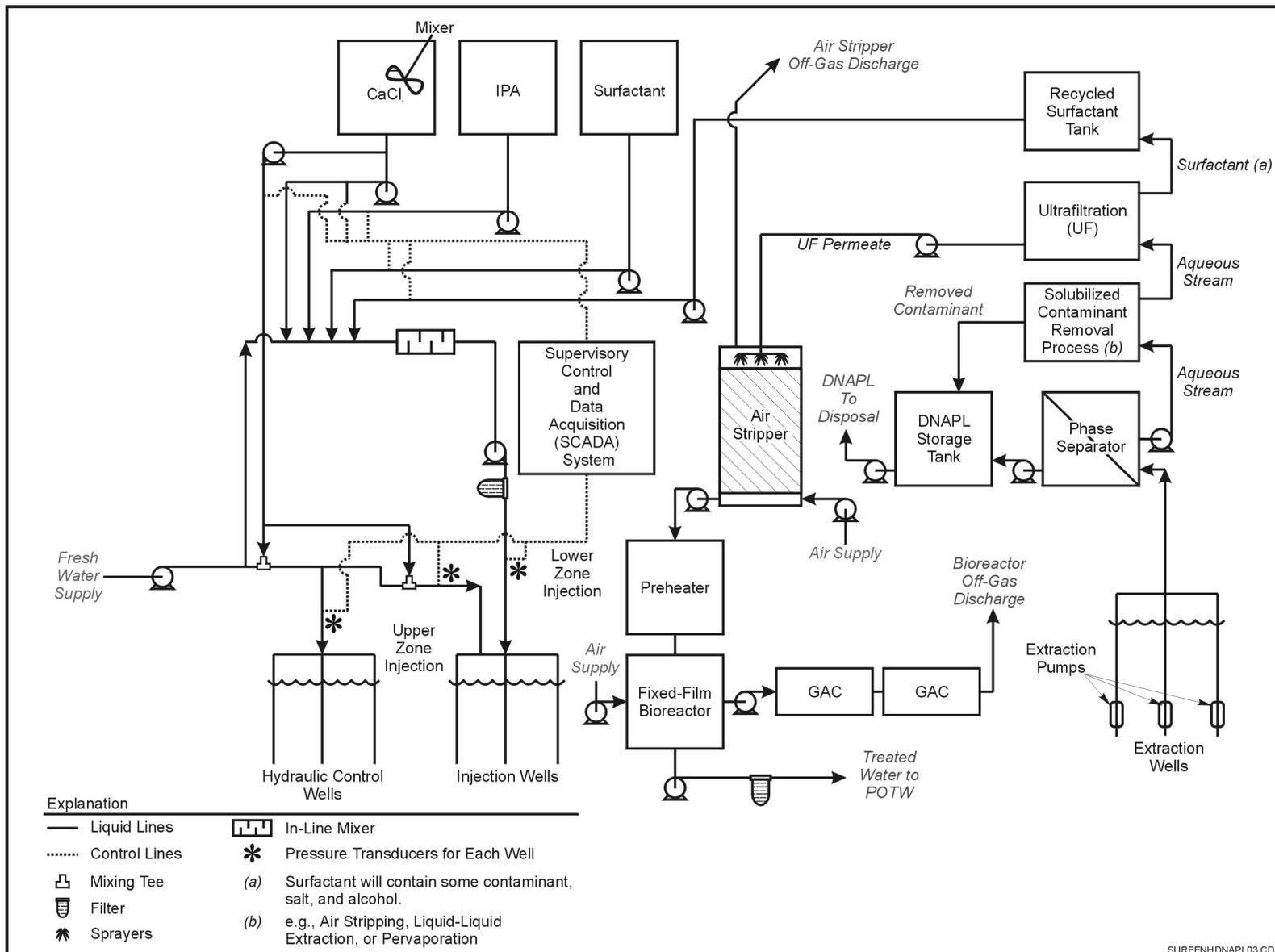
Figure 6-1. Conceptual Diagram of Full-Scale SEAR System with Surfactant Recovery

Table 6-6. Cost and Savings Estimates for Surfactant Recovery at a Site with Parameters Similar to Site 88, MCB Camp Lejeune

Cost and Savings	Low k			High k		
	1 panel	0.5 acre	1 acre	1 panel	0.5 acre	1.0 acre
Cost of Recovery Technologies	($ 259,900)	($ 580,600)	($1,015,600)	($82,400)	($252,400)	($381,900)
Value of Recovered Surfactant	$63,000	$ 588,400	$ 1,260,924	$33,600	$ 224,200	$ 493,200
Cost of Additional Tankage & Pumps[a]	($10,300)	($66,900)	($75,700)	($2,700)	($10,900)	($19,000)
Cost of Additional Analyses	($5,800)	($46,400)	($92,800)	($7,500)	($17,780)	($35,660)
Cost of Additional Labor	($230)	($1,840)	($3,680)	($230)	($1,840)	($3,680)
Credited Cost[b]	$ 91,300	$ 102,800	$ 115,900	$ 90,200	$ 92,400	$ 95,100
Total Net Cost Savings	($121,930)	($4,540)	$189,044	$30,970	$33,680	$148,060

(a) The 21,000 gallon steel tanks are rented and the 12,000 gallon plastic tanks are purchased. All pumps are purchased and include utilities costs for the ½ the surfactant flood period.
(b) This credits the cost of the air-stripper off-gas treatment unit associated with the conventional wastewater treatment system.

compounds (CVOCs). The resistive heating cost estimate was based on application of six-phase heating (SPH™) by Current Environmental Solutions (CES), Inc., (Fleming, 2000). SPH™ uses an array of electrodes installed in the ground to generate resistive heating of the soil and groundwater. The DNAPL is volatilized to the vadose zone and captured by means of a vapor extraction system. In both technologies, the fluids recovered aboveground require additional treatment before they are discharged to a sewer. By the very nature of their application, both steam injection and resistive heating will treat the entire 11 ft of aquifer, not just the bottom 5 ft. Neither of the two vendors contacted indicated any additional technology-specific characterization requirements, beyond what may have already been done to delineate the hydrogeology and DNAPL distribution in the source region.

Table 6-7 summarizes the total cost of SEAR and other alternative technologies considered for remediation of the DNAPL source zone at Site 88, MCB Camp Lejeune. All three alternatives (and SEAR) have been used previously at various sites for DNAPL source remediation; however, their relative technical merits under different site conditions may vary and their performance advantages/limitations have not been considered in this level of cost evaluation. It also is assumed that SEAR and the alternative thermal technologies will treat the DNAPL source zone to a point where natural attenuation will be able to address any residual plume; this assumption does not apply to the P&T technology as it is intended to achieve containment rather than remediation. The post-treatment cost of monitored natural attenuation is not included for any of the technologies. For any of the technologies under consideration, costs of pre- and post-treatment site characterization of the DNAPL source have not been included. It is assumed that the site owners will bear the cost of pre- and post-treatment characterization, and that technology vendors will be presented with a well-characterized site.

Table 6-7. Summary of SEAR and Alternative Technology Costs for Full-Scale Application for Remediation of the DNAPL Source Zone at Site 88, MCB Camp Lejeune

Cost Category	SEAR[a]	P&T System[a]	Steam Injection[a]	Resistive Heating[a]
Capital Investment	$890,000	$120,000	$702,000	$347,000
Contaminant Disposal Costs	$3,800	$30,000[b]	$90,000	$94,000
O&M Cost[c]	$ 498,100	$1,385,000[b]	$403,000	$198,000
Total (PV) Cost	**$1,391,900**	**$1,535,000[c]**	**$1,195,000**	**$639,000**

(a) All costs rounded to the nearest thousand. Post-remediation action required to control any residual plume is not included. Costs of site characterization of the DNAPL source zone before or after treatment is not included for any technology.

(b) $1,415,000 ($1,385,000 O&M cost and $30,000 contaminant disposal cost) is the undiscounted (rate of return = 0) PV of the recurring and periodic O&M costs in today's dollars spread over 30 years of operation. This total includes $45,000 of recurring annual operating and maintenance (O&M) cost incurred in every year of operation, $13,000 in periodic maintenance costs incurred every 10 years, and $13,000 in periodic maintenance costs incurred every 20 years.

(c) O&M costs not including contaminant disposal.

(d) $1,535,000 is the undiscounted (rate of return = 0) PV cost over 30 years of operation. This total is the sum of the initial capital invested and the annual real costs over 30 years. If P&T were to be continued for 100 years, the total undiscounted PV cost would be almost $5 million.

SEAR, steam injection, and resistive heating are source remediation technologies with applications that can be completed in a few months. P&T is a long-term source control technology and the total cost for this option is based on the present value (PV) of all the costs incurred over a 30-year period of application.

Further details of the cost estimates provided above for pump and treat, steam injection and resistive heating can be found in Appendix I (Battelle, 2000).

Section 7.0: REGULATORY ISSUES

7.1   Approach to Regulatory Compliance and Acceptance

The SEAR technology and the ESTCP project objectives were discussed with the North Carolina and regional EPA regulators prior to the selection of Site 88, MCB Camp Lejeune, North Carolina as the demonstration site. As mentioned in Section 3.1, the favorable response from the regulatory team for MCB Camp Lejeune, particularly on the issue of surfactant recycle, was one of the reasons Site 88 was selected as the demonstration site. Throughout all stages of the project, from the initial DNAPL investigations to the design and planning efforts, any issues requiring regulatory input, such as flexibility in meeting the State of North Carolina's 95% contaminant standard, were closely coordinated with the appropriate regulators. In addition, the community was informed of the SEAR activities at Site 88 via the MCB Camp Lejeune Restoration Advisory Board (RAB), a body composed of members from the public, regulators and Navy and Marine Corps environmental restoration personnel. During the SEAR demonstration, a visitor's day event was conducted to familiarize regulators, contractors and other interested parties with SEAR setup and operations. A separate site tour was also provided to RAB members.

Following the demonstration, the regulators were given a comprehensive presentation of the results and thus gained an understanding of the applicability and limitations of SEAR at a shallow, low permeability site such as Site 88. However, the Site 88 surfactant flood demonstration also contributed to an unfavorable cost perception of the technology. There are several reasons for the relatively high cost of the SEAR demonstration including the following:

- SEAR costs are higher for applications at low permeability sites (10^{-4} to 10^{-5} cm/sec) such as Camp Lejeune relative to higher permeability sites ($\sim 10^{-3}$ cm/sec) such as Hill AFB. This is readily apparent from the costs presented in Tables 6-3 and 6-4, which indicate that at a site with the dimensions of Site 88, high permeability conditions would cost 68% as much to treat as low permeability conditions. As the volume of the contaminated zone increases, the economies of scale favor the high permeability site, with the high permeability SEAR costs representing about 35%-40% of the low permeability SEAR costs.

- The costs for this SEAR demonstration were notably higher to meet the data quality objectives of technology verification than would be required strictly for remediation alone.

SEAR performance did not meet original expectations, i.e., the 70% DNAPL removal efficiency fell short of the target 97% contaminant removal. This was due to a higher degree of heterogeneity within the contaminated sediments than indicated by aquifer characterization measurements used to design the surfactant flood. Next, the DNAPL contamination at Site 88 currently poses low risk to drinking water resources. This can be attributed to the presence of a thick aquitard underlying the DNAPL contamination, which separates the DNAPL-contaminated shallow aquifer from the underlying drinking water aquifer. Finally, there has been some discussion of terminating dry-cleaning operations at Site 88 and removing the building. In this case, excavation and disposal of the DNAPL contaminated sediments or the use of thermal technologies may be feasible and more economical than the use of surfactants.

Subsurface recovery of injected SEAR chemicals was less than the minimum target of 90% for each component, however, there have been no concerns with the residual surfactant or IPA left in the ground at Site 88. Similarly, there have been no regulatory requirements imposed for post-SEAR groundwater monitoring. It is expected that regulatory controls on chemicals remaining in the ground following a SEAR demonstration will vary from site to site and depend on factors such as the proximity of the source zone to drinking water or other protected water sources (wetlands etc.).

Regulators were willing to be lenient on the 95% contaminant removal standard required for surfactant reinjection due to planning phase discussions where the project team established that: (1) good hydraulic control of the system based on CITT and PITT results would be maintained and that (2) the concentrations of contaminant being injected would be lower than the contaminant concentrations remaining within the aquifer. Although (2) was not actually met for Varsol™ during the SEAR demonstration, the regulators had also requested collection of pre- and post-SEAR groundwater samples for Varsol™ analysis to confirm that SEAR, although not targeted to remove Varsol™ from the aquifer, did not worsen Varsol™ contamination in the groundwater. Table 9-11 of the App G report shows pre- and post-Varsol™ concentration data for five well locations. By request of the NC regulators, five analytical methods for petroleum hydrocarbon identification were used to confirm that SEAR, although not targeted to remove Varsol™ from the aquifer, did not worsen the existing Varsol™ contamination. According to the Extractable Petroleum Hydrocarbon (EPH) method, as well as the Gasoline Range Organics (GRO) method results for the aromatic fraction, the Varsol™ concentrations decreased in all wells. However, according to the Volatile Petroleum Hydrocarbon (VPH) and GRO methods, there was a slight increase in C9-C12 aliphatic components of Varsol™ at two of the five monitoring locations. The VPH method also shows an increase in C5-C8 range aliphatics at four of the five monitoring locations, however, because C5-C8 aliphatic compounds were not monitored during the SEAR demonstration, it is not possible to comment on the effect of SEAR on these results. The greatest increase in C9-C12 compounds occurred at EX02, with VPH-measured concentrations increasing from 756 μg/l to 1400 μg/l. At this same location, GRO-measured concentrations increased from 240 μg/l to 630 μg/l, but the method does not distinguish the carbon number of the aliphatic compounds. While it is possible that the slight increase in C9-C12 compounds is due to reinjection of Varsol™ compounds at concentrations higher than in the aquifer, the marker compounds monitored during the SEAR recovery operations, i.e., decane (C10) and undecane (C11), showed high affinity for and thus a tendency to remain with the surfactant. Biodegradation of the Alfoterra 145-4PO sulfate™ surfactant has been hypothesized but is unlikely to have contributed to the increase in aliphatic compounds that has been observed. Therefore, it is difficult to resolve the discrepancies between the different methods; however, all results considered, SEAR treatment does not appear to have had much impact on Varsol™ concentrations in the aquifer.

Section 8.0: TECHNOLOGY IMPLEMENTATION

8.1   DoD Need

In their development of the National Action Plan for DNAPL Source Reduction, the Federal Remediation Technologies Roundtable estimated that DNAPL is present at 60%-70% of Superfund National Priorities List (NPL) sites (EPA, 2000b). Since there are currently about 100 NPL sites within the Department of Defense (Source: U.S. EPA Superfund Site Information, 2000), this translates to 60-70 DNAPL sites, if only NPL sites are included. Without detailed investigation, it is not possible to definitely determine the applicability of surfactant flooding to these DNAPL sites; however, a conservative estimate is that surfactant flooding is technically feasible at 30% or more of these DNAPL sites. This assumes that the DNAPL exists in the saturated zone, that surfactant flooding has no technical limitation with respect to the contaminant type, that hydraulic control of the injected chemicals and mobilized DNAPL can be maintained, and that there is sufficient permeability to inject surfactants.

8.2   Transition

The SEAR technology would benefit from further demonstration at a larger-scale to address the challenges (e.g., technology design, implementation and performance) of full-scale remediation at the largest scale possible, but minimally 4-5 times the scale of the Camp Lejeune demonstration. Additionally, in future demonstrations, all of the DNAPL contamination existing in hydrogeologically connected areas at a site should be addressed rather than a small portion of the total DNAPL zone; this avoids inaccuracies in performance assessment measures caused by reinfiltration of DNAPL into remediated areas from untreated areas. Targeting removal of the entire source also makes site closeout possible, which is the best outcome for the use of source-zone removal technologies. Along a similar line of thought, any demonstration that combines the SEAR technology with a follow-on technology (i.e., subsurface treatment train) that achieves groundwater remediation standards is of greater value than the SEAR technology alone. Finally, as shown in Section 6.1, the unit cost of SEAR technology implementation would potentially benefit from application at a larger scale, assuming that technology performance is comparable to or better than technology application at a smaller scale.
The SEAR demonstration at MCB Camp Lejeune, North Carolina, was conducted without industry involvement. Organizations, such as Dupont, have expressed an interest in the SEAR technology, but have also voiced concerns regarding the high cost of technology implementation, particularly at their larger sites. A larger scale demonstration would be most feasible to conduct with industry partners. One possibility is conducting the demonstration at an industry site, with the bulk of remediation costs borne by the industry client, federal funding of performance assessment measures conducted before, during and following SEAR remediation, and leveraged funds in equipment and/or labor from the technology vendor.

Throughout the execution of this ESTCP project, NFESC has engaged in a number of activities to disseminate information on the SEAR technology. A presentation of DNAPL site characterization methods and the SEAR technology was conducted at six Navy Engineering Field Divisions during the Spring 1998 Remedial Innovative Technologies Seminar (RITS). Additionally, numerous technical presentations (totaling over 20) on SEAR design and remediation, as well as on the ESTCP demonstration at MCB Camp Lejeune, have been given at technical conferences and meetings. Recently, NFESC has prepared a tri-fold brochure with basic information about SEAR. A two-part SEAR guidance document, funded by ESTCP and NFESC, is in progress. The first volume addresses SEAR design, while the second volume discusses SEAR implementation. This will be the first published document that focuses on the practical aspects of SEAR application for DNAPL removal. The two-

volume SEAR guidance document will be made available on the NFESC website. Furthermore, two workshops have been conducted based on the SEAR guidance documents. The first one was held in conjunction with the Battelle Chlorinated and Recalcitrant Compounds Conference in Monterey, California on May 21, 2000. Another was held in connection with the Interstate Technology and Regulatory Cooperation Work Group (ITRC) Fall Conference in San Antonio, TX on October 15, 2000. In addition to the above-mentioned ongoing activities, effective technology transfer will necessitate coordination with other federal agencies and workgroups, e.g., the Federal Remediation Technologies Roundtable (FRTR), and the Remediation Technologies Development Forum (RTDF).

The widespread use of SEAR necessitates the development of standard parameters that define successful application of the technology. An optimistic viewpoint is that any mass removal is beneficial as it represents a reduction in risk to the ecology and the environment. An alternate viewpoint is that if >99% contaminant removal is not achieved, that the technology has not been successful, as the 1% contamination remaining may still prevent the accomplishment of cleanup goals that allow the site to be closed out. Certainly this latter viewpoint would prevent investment in any DNAPL removal technology; hence the importance of working with the regulatory agencies to develop reasonable endpoint criteria for the use of source removal technologies. The need to design for removal of all DNAPL from even the lowest permeability zones should be evaluated against risk based site-specific conditions. This concept has been propagated recently in terms of the mass flux reduction or removal of DNAPL mass from the most permeable and transmissive zones of the aquifer (Enfield, 2000). A strategy such as this will of course require the development of consistent methods for measuring mass flux from various portions of the aquifer. This measurement criteria is already in use for NAPL sites in Germany (Teutsch, 1999). Finally, with or without the formulation of standardized performance parameters, the development of inexpensive and accurate technologies for assessing pre and post treatment DNAPL saturations will be essential to performing meaningful evaluations of SEAR and alternative DNAPL remediation technologies.

Section 9.0: LESSONS LEARNED

There were several lessons learned during the field demonstration conducted at Site 88 that will assist in future implementation of surfactant flooding technology at other sites. These are discussed below in the form of problems identified and suggested remedies.

Permeability Constraints Impact SEAR Performance and Cost. This ESTCP demonstration investigated the permeability constraints associated with implementing SEAR, both in terms of the absolute permeability as well as the permeability contrast when sited in a shallow, thin aquifer. Based on the costs in Tables 6-3 and 6-4, it is significantly more expensive to apply the SEAR technology when permeabilities are lower than 10^{-4} cm/sec. Although low permeability sites such as Camp Lejeune are not necessarily the norm, sites with significant heterogeneities in permeability are common. Such heterogeneities in permeability will adversely affect SEAR performance unless properly characterized and accounted for in the design. The Camp Lejeune project has shown the difficulties associated with conventional methods of quantifying changes in permeability within an aquifer. Aquifer testing only provides an estimate of bulk hydraulic conductivity, while MLSs are subject to failure, particularly when installed in zones of low permeability sediments. Although grain-size analyses conducted during the post-SEAR soil sampling provided useful data regarding the true permeability contrast, which supports observations and results from the SEAR test, it is an empirical approach that requires some foresight in the selection of sampling locations. For these reasons, a robust SEAR design that can overcome shortcomings of source-zone characterization is highly desirable.

Use of Mobility Control is Recommended. The solution to a robust SEAR design is the inclusion of mobility control measures. Due to recent advancements in SEAR design, mobility control is now considered an integral component of SEAR design and implementation because it improves the effectiveness of SEAR in two important ways: (1) it significantly mitigates the effects of heterogeneities with respect to remedial performance, and (2) decreases costs, primarily by reducing the amount of surfactant required. Under shallow conditions (20-25 ft to the bottom of the contaminated zone), the minimum bulk hydraulic conductivity needed to permit an efficient sweep of a high viscosity polymer-surfactant solution is approximately 10^{-3} cm/sec. A minimum depth of 50 ft is recommended for lower bulk hydraulic conductivities. This additional depth, or aquifer thickness, allows a greater range of hydraulic gradients to be imposed by the injection and extraction wells during flooding operations, which is needed to drive the higher viscosity polymer-surfactant solution through a low-permeability formation. The use of surfactant–foam processes for mobility control will additionally be limited by the composition of the surfactant formulation, i.e., when cosolvent is a component, surfactant-foam processes can not be used due to the defoaming properties of cosolvents. For optimum system performance, mobility control measures that can improve the sweep of surfactants through the low permeability zones of a heterogeneous aquifer are highly recommended in the design of all future SEAR projects. If the hydrogeologic setting at a given site will not allow the use of mobility control, then as the Camp Lejeune results indicate, inefficient performance and increased costs can be expected.

Geostatistics Should Be Used To Improve Performance Assessment. The minimum number of soil samples necessary to generate an accurate DNAPL volume estimate was one of the issues identified regarding the accuracy of using conventional technologies to quantify pre- and post-SEAR DNAPL saturations. The collection of 60 soil samples to estimate the DNAPL volume in 111 cubic yards of soil may be considered by many to be excessive; however, as discussed in Section 5.2, using geostatistics we have demonstrated that it is close to the minimum number of samples necessary. That this number represents a greater number of samples than usual raises questions about technology performance claims made about other demonstrations that were based on an inadequate number of soil

samples collected before and after treatment. As discussed in Section 6.0, cost data for a given technology are not meaningful when performance data are weak or unavailable for a given contaminated matrix.

Limitations to PITT Application Were Experienced. Issues were raised regarding the permeability limitations of PITTs and the surfactant components as a potential source of interference to a PITT in obtaining an accurate estimate of post-SEAR DNAPL volumes. The underestimate of the initial DNAPL volume during the pre-SEAR PITT, as well as the lower than expected tracer recoveries in both the pre- and post-SEAR PITT suggest limitations in implementing PITTs in an aquifer with low bulk permeability plus significant permeability contrast. These limitations should be considered in future decisions in using and designing PITTs. To meet the dual objectives for injection in low permeability soils and recycleability using membrane processes, a custom surfactant (Alfoterra 145-4PO sulfate™) was developed for the Camp Lejeune demonstration. However, the presence of impurities in this surfactant caused some surfactant sorption in the subsurface that led to a lower surfactant recovery than desired, and also caused interference with the partitioning tracers used to quantify the DNAPL distribution in the aquifer. The high organic content of the Camp Lejeune soils and the natural tendency of partitioning tracers to sorb to these soils masked the sorbing effect of the surfactant impurity during laboratory surfactant testing. Thus, in future efforts to examine the interfering effects of surfactant impurities, laboratory experiment should include the use of clean Ottawa sands. Additionally when designing PITTs in an aquifer with significant clay content that necessitates calcium as the primary electrolyte, tendencies of surfactants to form complexes with calcium-containing clays should be carefully examined for proper surfactant flood design to avoid interfering effects with the PITT.

Proper Well Development is Key to SEAR Performance. SEAR wells are crucial components of the remediation system since surfactant fluids are controlled in the subsurface via injection, extraction and hydraulic control wells. As such, SEAR wells should be thought of as performance wells, with very different specifications compared to monitoring wells. Conventional well installation methods should be strictly followed for SEAR wells, including proper screen length and placement, appropriate screen slot size, continuous-slot screens, and appropriate filter pack material (see Driscoll, 1995). Following proper installation, vigorous well development is very important for maximizing the well efficiency of the remediation wells. This ensures that the maximum range of injection and extraction flow conditions can be applied across the well field, which is especially important for surfactant flooding a shallow aquifer with tight sediments. Effective well development can be accomplished by vigorous surging and pumping, which needs to be emphasized with the driller prior to mobilizing to the field for well installation. While this task was included in the driller's scope of work for the Camp Lejeune well installations, the surge block supplied by the driller was not properly designed for effective well development. Consequently, one extraction well installed in a known free-phase DNAPL zone yielded no DNAPL and was replaced. Hydraulic control well HC-01 received less well development because it was situated inside of a building that did not allow access of a drilling rig for vigorous surging. With the hand-surging performed, its efficiency was expected to be less than for other wells. This may have been a contributing factor to the temporary loss of hydraulic control at RW-03 when injection and extraction flowrates were increased during Phase II of the surfactant flood.

Focused Well Placement Is Recommended. Another recommendation for optimizing the future performance of surfactant floods in aquifers with appreciable permeability contrasts such as Camp Lejeune is to install separate arrays of injection and extraction wells that are discretely screened over the particular aquifer zone requiring improved sweep. For example, at Camp Lejeune, an additional injection well could be installed at each injection location, with a screen over the lowest permeability zone (bottom 1.5 to 2 feet) of the aquifer to focus the flow of surfactant fluids through this zone. A likely

implementation of this technique would be to install 2 arrays of cone penetrometer test (CPT) well-points, one array screened in the overlying higher permeability zone and the other array screened in the basal silt layer. Where depth is not a limiting factor for the installation of horizontal wells, the use of horizontal and vertical wells in a hybrid arrangement (i.e. horizontal injection wells/vertical extraction wells or vice versa) may hold some benefit for treating aquifers with high permeability contrasts. Site-specific design modeling is necessary to determine whether a benefit exists and the optimum well configuration.

Surfactant Formulation Can Be Improved. The range of $CaCl_2$ concentrations to maintain Winsor Type III conditions that maximizes contaminant solubilization and IFT reduction by surfactant was too narrow (between 0.18 wt% to 0.20 wt% $CaCl_2$), to use the surfactant at optimum efficiency without risking undesirable Winsor Type II conditions that result in surfactant loss into DNAPL; thus, the average calcium concentration used was lower than optimum, around 0.17 wt%. Solubilization of PCE at 0.17 wt% and 0.185 wt% calcium by the Alfoterra 145-4PO sulfate™ surfactant is 400,000 and 500,000 mg/L PCE, respectively. Therefore, operating at 0.17 wt% $CaCl_2$ is equivalent to a 20% loss of solubilization potential. A lesson learned from this demonstration is that it is preferable to use surfactants with a wider range of Type III phase behavior (i.e., a wider range of electrolyte concentrations for Type III phase behavior). The use of on-line metering and mixing of surfactant formulation components for the preparation of surfactant injectate is also recommended for improved precision and accuracy of the surfactant formulation. However, phase behavior experiments must still be performed regularly by qualified personnel to verify that surfactant injectate meets design specifications during field operations.

The high residual IPA concentrations (up to 44,000 mg/L) remaining in the SEAR treatment zone approximately 18 months after the completion of the demonstration imply that the use of surfactants requiring high cosolvent concentrations, should be reconsidered in future SEAR applications. Cosolvents also complicate SEAR effluent treatment and prevent the use of surfactant-foam for mobility control. Newly developed surfactants such as the Alfoterra 123-8PO sulfate™ and Alfoterra I12-3PO sulfate™ that minimize the cosolvent requirement, or other surfactants that might be identified in the future that can be used without any cosolvent should receive preference. In addition, co-surfactants have recently emerged as substitutes for cosolvents in surfactant systems, and should be explored further.

Additional Technology Development May Benefit the Economics of Surfactant Recovery. The unintended concentration of calcium and residual contaminant was an issue during MEUF treatment to recover surfactants. The necessity of diluting the recovered surfactant with fresh surfactant to adjust calcium and contaminant concentrations to appropriate levels decreased the value of the recovered surfactant. Ion exchange treatment was examined as a potential solution to remove excess calcium, but at the current state is not an economical alternative. When surfactant recovery is 60% or less, and multiple panels are being remediated, dilution by fresh surfactant does not represent a huge loss of reusable surfactant, as it only impacts the final panel. It should also be kept in mind that not all sites will require the sole use of calcium chloride as the electrolyte to avoid the mobilization of soil fines, and that electrolyte concentration will not be a concern at every site. Yet, when surfactant recovery is more efficient and/or only a single panel is being remediated, the impact of excess calcium concentrations can impact the economics of surfactant recovery significantly. Therefore additional investigation of methods to prevent or address calcium electrolyte concentration is warranted. Contaminant concentration by MEUF will be a more universal phenomenon and requires that any surfactant-contaminant separation process achieve higher contaminant removals. For example, if contaminants are concentrated 5-fold by MEUF, then to meet a 95% contaminant removal, the contaminant removal process must remove 99% of the contaminant initially so that the 1% contaminant remaining will be concentrated up to 5% during

surfactant recovery via ultrafiltration. Additionally, the Camp Lejeune demonstration showed that the composition of the extraction well effluent can vary significantly from design values; therefore, any process used to separate contaminant from surfactant should have flexibility in design and operation to treat an influent stream with fluctuating surfactant and contaminant concentrations, especially higher concentrations of either component that will tend to worsen contaminant removal.

The results of the SEAR demonstration at Camp Lejeune underscore the difficulties in applying SEAR at a shallow, low permeability site, particularly when significant permeability contrasts are present. The SEAR design process at sub-optimal sites must consider all of the variables discussed above in order to improve the cost-effectiveness and success of SEAR implementation.

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APPENDIX A

POINTS OF CONTACT

APPENDIX B

DATA ARCHIVING AND DEMONSTRATION PLAN(S)

APPENDIX C

PHOTOGRAPHS OF THE SEAR DEMONSTRATION

APPENDIX D

POTENTIOMETRIC SURFACE MAPS FOR THE SEAR DEMONSTRATION

APPENDIX E

SURFACTANT, IPA AND PCE SAMPLING RESULTS AT MONITORING WELLS

APPENDIX F

SENSITIVITY ANALYSES ON CAMP LEJEUNE SOIL SAMPLES

APPENDIX G

SEAR FINAL REPORT
(See enclosed compact disc)

APPENDIX H

DETAILS OF ESTIMATED FULL-SCALE COSTS

APPENDIX I

ALTERNATIVE TECHNOLOGY COSTS FOR DNAPL SOURCE REMEDIATION AT SITE 88, MARINE CORPS BASE CAMP LEJEUNE