Final

DNAPL Site Chracterization Using a Partioning Interwell Tracer Test at Site 88, Marine Corps Base Camp Lejeune, North Carolina

Prepared for:

Department of the Navy:

Naval Facilities Engineering Service Center
Restoration Development Center
Port Hueneme, California

and

Naval Facilities Engineering Command
Atlantic Division
Norfolk, Virginia

Prepared by:

Duke Engineering & Services
Austin, Texas

In Cooperation with:

Baker Environmental, Inc.
Coraopolis, Pennsylvania

July 1999

Approved for public release; distribution is unlimited.

TABLE OF CONTENTS

LIST OF APPENDICES

LIST OF TABLES

LIST OF FIGURES

ACRONYMS AND ABBREVIATIONS

4M2P	4-methyl-2-pentanol
AST	above-ground storage tank
amsl	above mean sea level
Baker	Baker Environmental
bgs	below ground surface
Br^-	bromide
BTOC	below top-of-casing
C	concentration of tracer
$CaCl_2$	calcium chloride
CITT	conservative interwell tracer test
CLEAN	Comprehensive Long-Term Environmental Action Navy
CPT	cone penetrometer test
cm/sec	centimeters per second
DAS	data acquisition system
DCE	*cis*-1,2-dichloroethene
DE&S	Duke Engineering & Services
DNAPL	dense nonaqueous phase liquid
DOD	Department of Defense
DSI	Drilling Service Inc.
dyne/cm	dynes per centimeter
EPA	Environmental Protection Agency
ESTCP	Environmental Securities Technology Certification Program
FID	flame ionization detector
ft	feet
ft bgs	feet below ground surface
ft/day	feet per day
f_{oc}	fraction of sedimentary organic carbon in aquifer material (wt/wt)
gal	gallon
GC	gas chromatography
g/cm^3	grams per cubic centimeter
gpm	gallons per minute
IFT	interfacial tension
in	inch
IRP	Installation Restoration Program
kg/m^3	kilogram per cubic meter
k_{avg}	average permeability
K	hydraulic conductivity
K_i	partition coefficient for the i^{th} tracer

Acronyms and Abbreviations, Continued

K_n	partition coefficient for a non-partitioning tracer
K_p	partition coefficient for a partitioning tracer
LANTDIV	Atlantic Division, Naval Facilities Engineering Command
lb	pound
LNAPL	light nonaqueous phase liquid
m	meter
m/s^2	meters per seconds squared
µm	micrometer
MCB	Marine Corps Base
MLS	multilevel sampler
µg/L	micrograms per liter
µg/Kg	micrograms per kilogram
mg/Kg	milligrams per kilogram
mg/L	milligrams per liter
mL	milliliter
NAPL	nonaqueous phase liquid
NAVFAC	Naval Facilities Engineering Command
NFESC	Naval Facilities Engineering Service Center
NRMRL	National Risk Management Research Laboratory
OHM	OHM Remediation Services Corporation
PA	performance assessment
PCE	tetrachloroethene (i.e., perchloroethylene)
PID	photo-ionization detector
PITT	partitioning interwell tracer test
ppb	parts per billion
ppm	parts per million
Q	flow rate
QA/QC	quality assurance/quality control
RAC	Remedial Action Contractor
RI	Remedial Investigation
SEAR	surfactant-enhanced aquifer remediation
SOP	Standard Operating Procedure
TCE	trichloroethene
UST	underground storage tank
VOC	volatile organic compound
XRD	X-ray diffraction

EXECUTIVE SUMMARY

A partitioning interwell tracer test (PITT) was recently completed at Site 88, the location of the Morale, Welfare, and Recreation (MWR) Dry Cleaners at the Marine Corps Base (MCB) Camp Lejeune, North Carolina. This PITT was conducted to estimate the saturation, volume, and spatial distribution of tetrachloroethene (PCE) that is present as a dense non-aqueous phase liquid (DNAPL) within the selected test area. The PITT results provide characterization of the initial DNAPL conditions at the site, in preparation for a surfactant-enhanced aquifer remediation (SEAR) demonstration to remove DNAPL from the surficial (shallow) aquifer at the site. The PITT is the most recent of many field investigations that have been conducted in the past year to characterize the DNAPL contamination at Site 88. The PITT data has confirmed the results of earlier soil and ground-water investigations, which indicated that the highest DNAPL saturations are located in the shallow aquifer regions adjacent to the dry-cleaning building, and within a layer of low-permeability sediments (i.e., clayey silt) just above a clay aquitard. A summary of the DNAPL investigations and other field activities conducted in conjunction with the PITT are provided in this report, along with the PITT results and data analysis.

The DNAPL source-zone investigations at MCB Camp Lejeune have been co-funded by the Environmental Securities and Technology Certification Program (ESTCP) and the Atlantic Division, Naval Facilities Engineering Command (LANTDIV), and were conducted in a teaming arrangement between Duke Engineering & Services and Baker Environmental (the LANTDIV CLEAN program contractor at Camp Lejeune). Additional site support was provided by OHM Remediation Services Corporation (the LANTDIV RAC program contractor at Camp Lejeune). These investigations proceeded in three phases, as described below.

- Phase 1: July – August, 1997

  The objectives of Phase 1 were to: (1) locate the DNAPL zone and (2) perform preliminary characterization of the DNAPL-contaminated geosystem (i.e., hydrostratigraphy, hydraulic and geochemical properties of the aquifer, and approximate DNAPL saturations). The Phase 1 investigation consisted of a small-scale soil-sampling program during which soil borings were pushed continuously to collect detailed lithologic data and soil samples were collected using in-field methanol preservation. This was followed by well installation to conduct hydraulic testing. Borings were completed beneath the building and around the building perimeter to a depth of about 21 feet below ground surface (ft bgs). Following the development of the newly installed wells, free-phase DNAPL was collected in two of the wells. The soil analytical results confirmed the presence of residual PCE DNAPL at a depth interval of approximately 17 to 20 ft bgs. Hydraulic testing

demonstrated that the aquifer soils had sufficient permeability for implementation of the SEAR technology.

- Phase 2: November-December, *1997*

  The objectives of Phase 2 were to: (1) roughly delineate the horizontal and vertical extent of DNAPL at the site, (2) establish baseline DNAPL saturations in the selected test area using soil borings and (3) perform additional site characterization to refine the geosystem model for the test well-field design. Phase 2 work combined laboratory and modeling studies to achieve the latter objective. The laboratory studies, using DNAPL and sediments collected from the site, resulted in the selection of a suite of tracers suitable for a PITT under site-specific conditions. Using site data gained from Phase 1 and 2 field investigations as input parameters, a geosystem model of the site was constructed using UTCHEM, a three-dimensional multi-phase flow simulator. Initial simulations with UTCHEM provided the optimum well geometry and spacing for the PITT and the subsequent surfactant flood. The designed well field, sited adjacent to Building 25, consists of a total of three injection and six extraction wells arranged in a 3X3X3 line-drive configuration, with a hydraulic control well located at each end of the row of injection wells. Thus, the test well field comprises 11 wells in total. The test area formed by the 3x3x3 array of injection and extraction wells is 20 ft wide by 30 ft long. Phase 2 activities culminated with the installation of the demonstration wells.

- Phase 3: January-July, 1998

  The objectives of Phase 3 were to measure the DNAPL volume and average saturations within the test zone with a PITT, in preparation for the SEAR demonstration. Phase 3 of the DNAPL source-zone investigation included field implementation of the PITT as well as preparatory field activities. First, free-phase DNAPL recovery was undertaken by means of pumping selected wells that showed DNAPL accumulation. This was followed by a water flood in the test-zone well field. An estimated 30-60 gallons of DNAPL was removed from the subsurface during the free-phase DNAPL recovery effort. Secondly, a conservative interwell tracer test (CITT) was conducted to evaluate the preliminary PITT design (i.e., flow rates, test duration) as determined by the Phase 2 design modeling. Using bromide as the tracer, tracer breakthrough was measured at the six extractor wells to determine the actual tracer residence time in the interwell swept pore volume between a given pair of injection and extraction wells. The results of the CITT showed that only minor revisions were needed in the initial design (i.e., injection and extraction flow rates) to finalize the PITT design.

  The PITT began on May 13, 1998, continued for 40 days, and terminated on June 22, 1998. Data analysis estimated that 74-88 gallons of DNAPL are present in the 4,800-gallon swept pore volume of the test zone. Average DNAPL saturations in the

test zone are highest in the area adjacent to the north wall of Building 25, at approximately 4% saturation, and decrease in a northerly direction away from the building to about 0.4% saturation at a distance of approximately 20 ft north of the building. However, the results of soil column studies conducted prior to the PITT suggest that the low-level DNAPL saturation (i.e. 0.4%) measured in the area located approximately 20 ft north of the building is actually the result of tracer sorption to sedimentary organic matter that is observable as peat particles in the sediments. Therefore the area of the test zone 20 ft north of the building is believed to be DNAPL free.

Phase 4, the SEAR demonstration began in April 1999 and is at the time of writing in progress (July 1999). The SEAR demonstration will be followed immediately by a second PITT to measure the volume of DNAPL remaining in the test zone. The results of the pre-SEAR and post-SEAR PITTs will be compared to assess the performance of the surfactant flood in removing DNAPL from the test zone at Site 88. This performance assessment of the SEAR demonstration will also determine the volume of DNAPL remaining in the test zone after the SEAR demonstration. Post-SEAR soil samples will also be collected from the test zone and analyzed for volatile organic compounds to provide additional evidence of the performance of the surfactant flood. The SEAR demonstration and post-SEAR PITT are scheduled for completion in late August 1999.

1.0 INTRODUCTION

A remedial investigation (RI) conducted by Baker Environmental (Baker) during 1996 to 1997 revealed the presence of dissolved phase tetrachloroethene (PCE) in the ground water at Operable Unit No. 15 (Site 88) at Marine Corps Base (MCB) Camp Lejeune, North Carolina (Baker; 1996,1998a). The location of Site 88 is shown in Figure 1.1, and is roughly defined as the area delineated by the extent of the aqueous phase PCE plume. The source of the PCE plume is the Base dry cleaning facility, which is housed in Morale, Welfare, and Recreation (MWR), Building 25. The PCE plume extends generally to the northwest and south from Building 25, as seen in Figure 1.2. Aqueous PCE concentrations were reported in the RI (Baker, 1998a) to range as high as 54.9 mg/L (54,882 µg/L; Figure 1.2) in the shallow aquifer, and also in the Upper Portion of the Castle Hayne Aquifer at concentrations up to 26.6 mg/L (26,592 µg/L; Figure 1.3). The Upper Portion of the Castle Hayne Aquifer has been used as a drinking water aquifer in the vicinity of MCB Camp Lejeune and nearby Jacksonville, NC. However, drinking water supplies do not currently appear to be threatened by the ground-water contaminants related to Site 88.

The RI was conducted by Baker Environmental (under the LANTDIV CLEAN [Comprehensive Long-Term Environmental Action Navy] program) for the Atlantic Division, Naval Facilities Engineering Command (LANTDIV) under the Installation Restoration Program (IRP) at MCB Camp Lejeune. Meanwhile, the Naval Facilities Engineering Service Center (NFESC), located in Port Hueneme, California, was searching for a site to conduct a field demonstration of surfactant-enhanced aquifer remediation (SEAR) with surfactant recycling and reinjection. The SEAR field demonstration is funded by the Department of Defense (DOD) under its Environmental Securities Technology Certification Program (ESTCP) in an effort to promote innovative technologies for effective remediation methods at DOD sites contaminated with dense, non-aqueous liquid (DNAPL). Chlorinated solvents, such as PCE and trichloroethene (TCE), when present in the subsurface as an immiscible liquid (i.e., DNAPL) slowly dissolve and provide a persistent source of aqueous contamination to the subsurface. Such sites are not cost-effectively remediated by traditional pump-and-treat methods (Mackay and Cherry, 1989).

The Site 88 RI reported aqueous PCE concentrations up to 54 mg/L present in the shallow aquifer, which is approximately 23% of the solubility of PCE based upon an aqueous solubility of 240 mg/L (Broholm and Feenstra, 1995; West, 1992). Such aqueous concentrations strongly suggest the presence of PCE DNAPL at Site 88. Based upon such evidence for the likelihood of DNAPL beneath Building 25, Site 88 was chosen by the ESTCP team, with support from LANTDIV, as a candidate site for

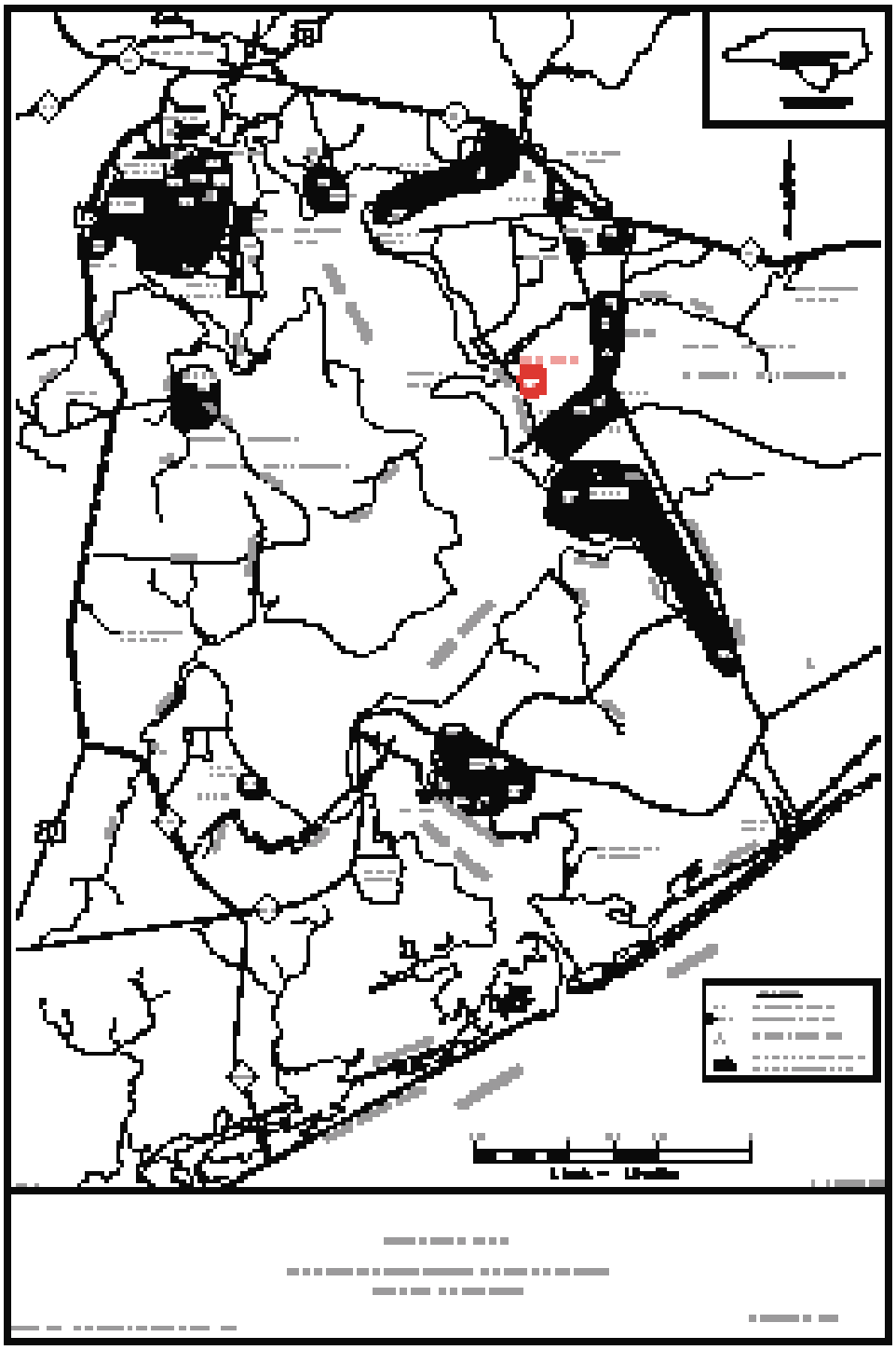

Figure 1.1. Location Map

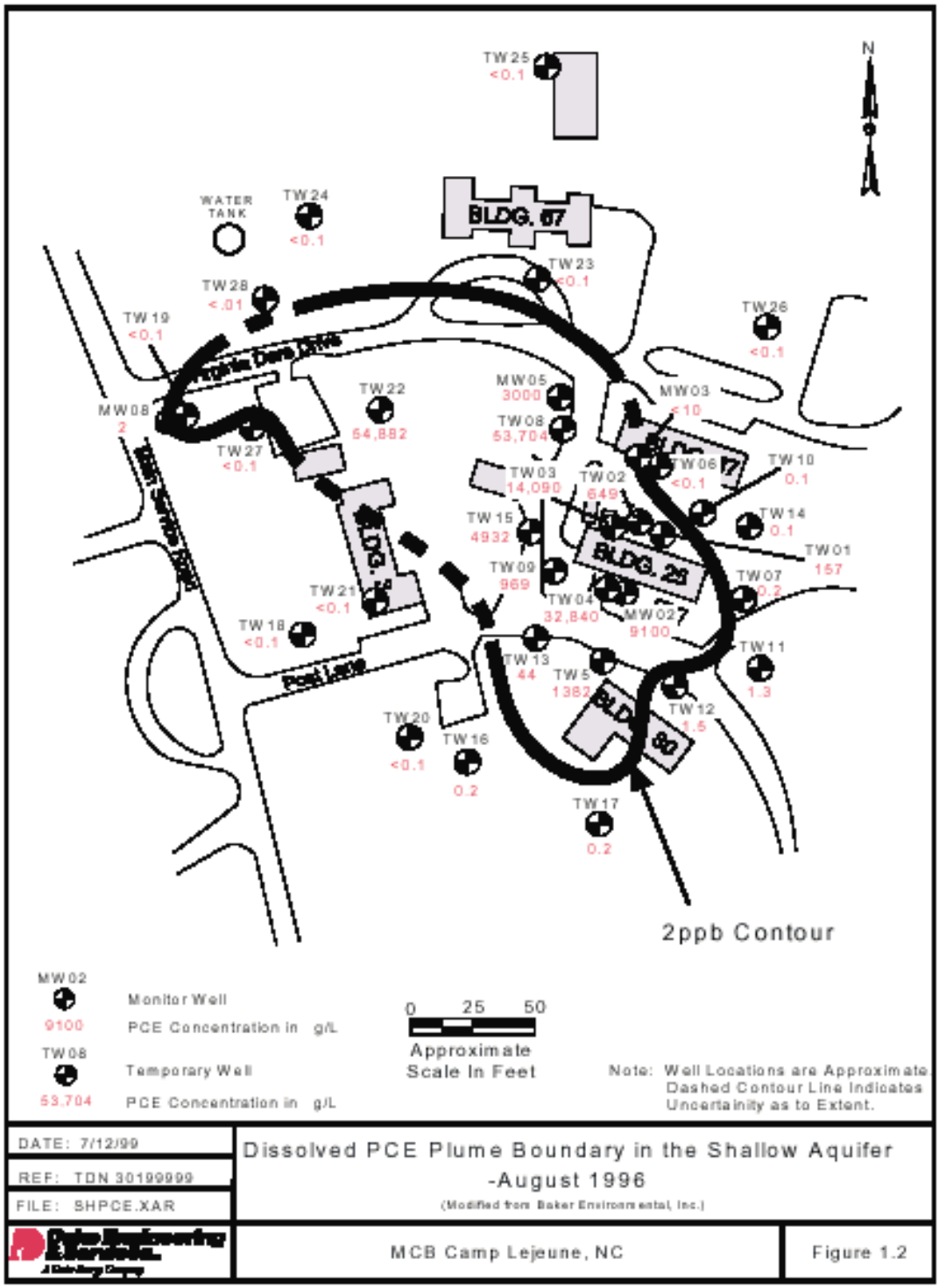

Figure 1.2. Dissolved PCE Plume Boundary in the Shallow Aquifer – August 1996

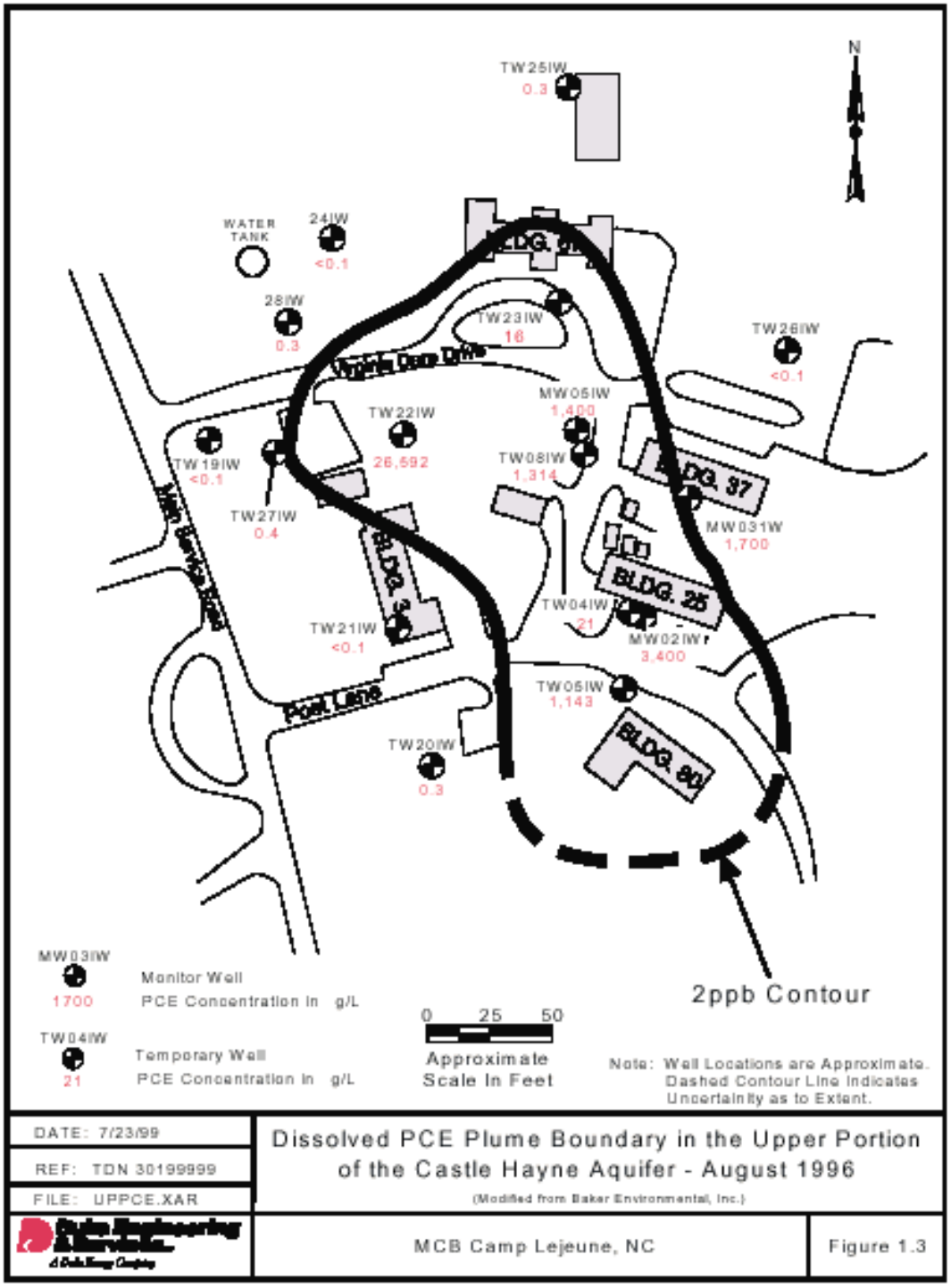

Figure 1.3. Dissolved PCE Plume Boundary in the Upper Portion of the Castle-Hayne Aquifer – August 1996

the ESTCP project pending the results of a preliminary DNAPL site investigation to locate the DNAPL zone beneath Building 25. This preliminary DNAPL source-zone investigation, conducted by Duke Engineering & Services (DE&S) in late 1997, in a teaming arrangement with Baker, confirmed the presence of DNAPL at Site 88. Two subsequent DNAPL investigations were then conducted to delineate the approximate extent of the DNAPL zone at Site 88, and to obtain estimates of aquifer hydraulic properties. The results of these preliminary DNAPL-zone investigations met the site-selection criteria for SEAR, therefore Site 88 was selected to be the demonstration site for the ESTCP project.

The purpose of this report is to summarize the PITT results as well as the results from all earlier DNAPL source-zone investigations conducted by DE&S at Site 88 in preparation for the upcoming SEAR demonstration.

1.1 Goals and Objectives

Performance assessment of the SEAR will be accomplished using PITTs. The PITTs will provide a quantitative comparison of the DNAPL volume and distribution in the test zone before and after the SEAR.

The goals of the pre-SEAR DNAPL investigations were to:

- define the geosystem of the test zone for the purpose of PITT and SEAR design, and;
- measure initial DNAPL conditions in the test zone with a PITT in preparation for the SEAR demonstration.

To meet the above goals, the specific objectives of the pre-SEAR DNAPL investigations were to design and conduct a PITT to:

- measure the total volume and average saturation of DNAPL in the test zone; and
- determine both the horizontal and vertical spatial distribution of DNAPL in the test zone.

1.2 DNAPL Occurrence and Definitions

PCE solvent is considered a DNAPL due to its relatively high density (1.63 g/cm^3) and immiscibility in water (interfacial tension in water = 47.48 dyn/cm; Demond and Lindner, 1993). If spilled in sufficient quantities, PCE DNAPL migrates downward from the

DNAPL entry location, through the vadose and saturated zones until stopped by a low-permeability barrier (i.e., capillary barrier), such as a clay. It can then migrate laterally downslope along the capillary barrier. As DNAPL flows through porous media, it leaves behind a trail of residual DNAPL that partially fills the pore spaces (see Figure 1.4). Residual DNAPL is held in the pore spaces by capillary forces and, due to its low solubility remains as a persistent source of contamination to the ground water. Free-phase DNAPL is defined as DNAPL existing in the subsurface under a positive pressure such that it can flow into a well (EPA, 1992). The Environmental Protection Agency (EPA, 1992) defines those areas containing residual or free-phase DNAPL as DNAPL zones.

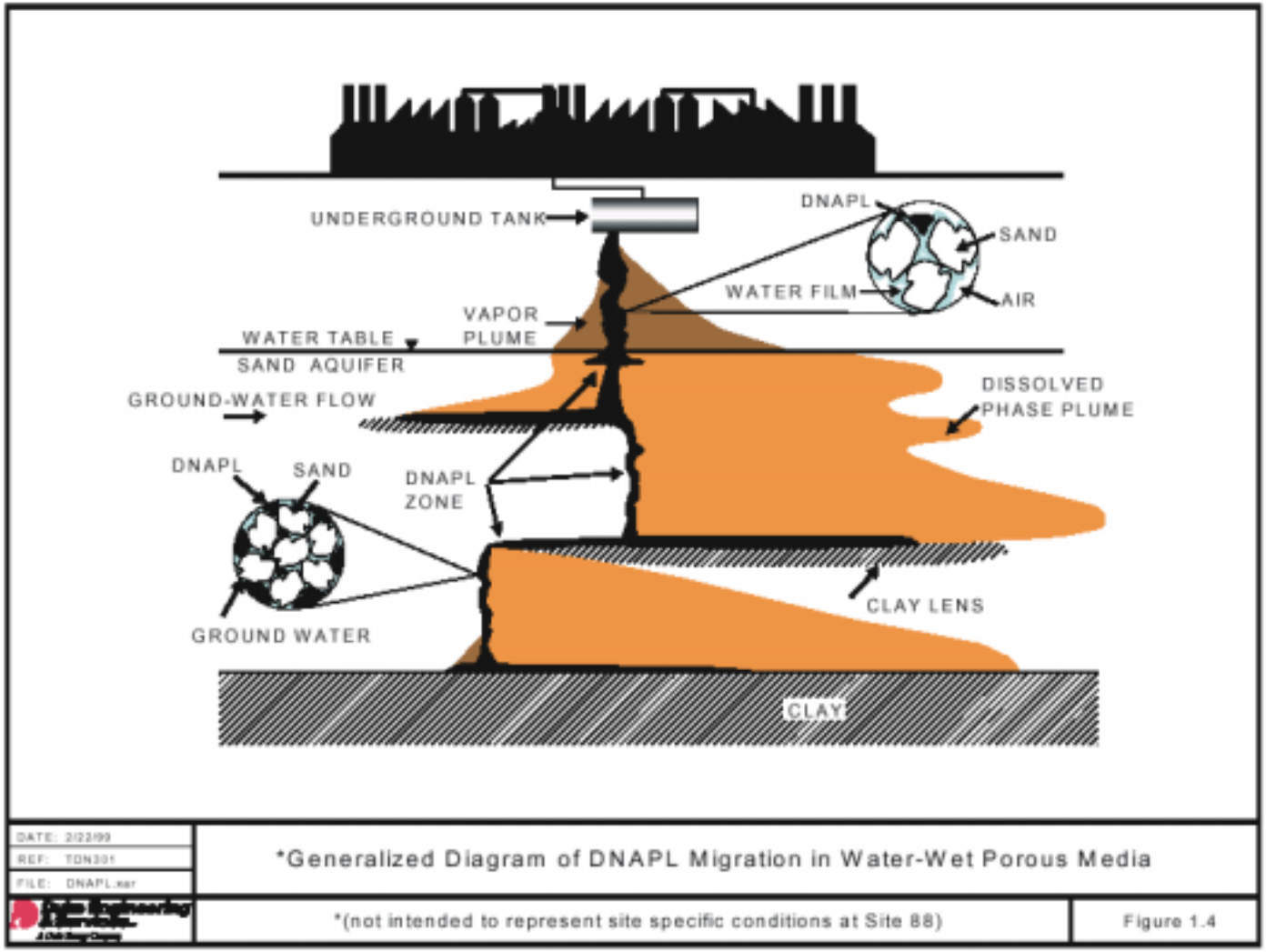

Figure 1.4. Generalized Diagram of DNAPL Migration in Water-Wet Porous Media

2.0 SITE BACKGROUND

This section provides a brief description of site historical operations, and general hydrology and hydrogeology for the Site 88 area. This information is provided to acquaint the reader with the general setting of Site 88. However, for more detailed information with respect to the hydrogeology of the SEAR demonstration area, see Section 5.0.

2.1 Site History

Building 25 has been operating as a dry cleaning facility since the 1940s. Varsol™, a petroleum distillate, or "mineral spirit", was used as the dry cleaning fluid from the 1940s through the 1970s. During the 1970s, due to the high flammability of Varsol™, the facility began to use PCE as the dry cleaning fluid. Varsol™ was stored in underground storage tanks (USTs) located on the northern side of the building. The Varsol™ USTs, most probably installed in the 1940s, were removed in November of 1995 by OHM Remediation Services (OHM). PCE was stored on site in the same vicinity as the Varsol™ but in 150-gallon above-ground storage tanks (ASTs).

At the time the USTs were removed in 1995, contamination of the soil and ground water was suspected. During informal interviews conducted during the DNAPL investigation, dry cleaning personnel indicated that historical operating practices included disposal of spent PCE into floor drains. The tanks, floor drains, and associated underground pipes may have provided conduits for contamination to reach the subsurface. The dry cleaners still use PCE, but current practices involve storing PCE in a 150-gallon self-contained AST that is located inside Building 25, and the dry cleaning machines are fully self-contained. The first such unit was brought on line in December 1986, and the second in March 1995.

2.2 Site Stratigraphy

A relatively uniform depositional sequence of sediments has been observed in borings across the site. The surficial aquifer, referred to as the shallow aquifer in this report, consists of fine to very-fine sands and silt which typify the sediments encountered from the surface to a depth of approximately 18 feet below ground surface (ft bgs). The shallow aquifer is bound below by a silty clay layer that varies in thickness across Site 88. Previous investigations have reported that the clay layer is laterally discontinuous in some areas of Site 88 (Baker, 1998a). However, the clay layer appears to be continuous in the vicinity of the DNAPL zone, as discussed in Section 5.0.

Beneath the clay layer is an interval composed of fine to medium sand with some silt to a depth of over 100 ft bgs, based on boring logs for monitor wells completed in the area (Baker, 1998a). This hydrostratigraphic unit is identified in the RI report as the Upper Portion of the Castle Hayne Aquifer (Baker, 1998a). In areas where the clay layer is not present, the shallow aquifer and Castle Hayne Aquifer are in direct hydraulic communication.

2.3 Hydrogeologic Setting

In the demonstration area, the water table varies annually from about 7-9 feet bgs, or about 16-18 feet above mean sea level (amsl), and the shallow aquifer is separated from the Upper Portion of the Castle Hayne Aquifer by the clay layer. As discussed above, the clay layer acts as an aquitard between the two hydrostratigraphic units. Core samples show that the clay layer is approximately 14-16 ft thick in the SEAR demonstration area. This aquitard core was collected through a surface casing, which was installed for the completion of a Castle Hayne Aquifer monitor well located in the DNAPL zone. Cone penetrometer tests conducted outside the DNAPL zone show the aquitard thinning towards the northeast and southwest of Building 25. Further discussion of the clay layer morphology is presented in Section 5.0 of this report.

Water levels in the Castle Hayne Aquifer are approximately seven feet lower than water levels in the shallow aquifer. The difference in water levels between the shallow aquifer and the Upper Portion of the Castle Hayne Aquifer, as well as the fact that DNAPL has pooled on the clay layer, are evidence of the competency of the clay layer as an aquitard in the demonstration area. In the vicinity of Building 25, the direction of ground-water flow in the shallow aquifer is generally to the southwest, which explains the southern extension of the plume from Building 25. However, the plume also extends in a north-northwesterly direction from Building 25 (see Figures 1.2 and 1.3). As mentioned in Section 2.1, historical operating practices at the dry cleaning facility included disposal of spent PCE into floor drains. Therefore, some PCE is suspected to have migrated via leaking sewer lines that flow in a north-northwesterly direction from Building 25. In areas of Site 88 away from Building 25, the ground-water flow direction is variable, as shown in the RI (Figure 3-7; Baker, 1998a) which may explain the complex shape of the PCE plume when considered in conjunction with the sewer line mechanism for lateral PCE migration from Building 25.

2.4 Surface Water

There are no surface water bodies in the immediate vicinity of the site. The nearest bodies of surface water to Site 88 are Beaverdam Creek and The New River, located about 1,500 ft northeast and 3,000 ft west, respectively, from the site.

2.5 Water Supply Wells

There are no active water supply wells located within a one-mile radius of the site. The nearest active water supply well is HP-642, which is located approximately 1.5 miles east of the site. There are no private wells within the confines of Camp Lejeune. All water on base is supplied by the Camp Lejeune water distribution system (analogous to a municipal water supply system).

The closest off-base property and hence the nearest possible private well, is approximately four miles northeast of Site 88.

3.0 DNAPL SOURCE-ZONE INVESTIGATIONS

DNAPL source-zone investigations were conducted in three phases at Site 88 to evaluate the site per NFESC criteria for the SEAR demonstration. The minimum criteria for site selection required that: (1) the site must be contaminated with a sufficient volume of DNAPL to provide a valid test of SEAR technology; and (2) the DNAPL zone must have sufficient permeability to support remediation via injection of surfactants and the subsequent recovery of the surfactant/DNAPL effluent at extraction wells within a reasonable period of time (i.e., economically justifiable timeframe).

Aquifer sediment samples (soil samples) were collected for volatile organic compound (VOC) analysis and for geologic logging during four separate drilling and sampling events to delineate the extent of the DNAPL zone and interpret the hydrostratigraphy of the DNAPL zone. The soil sampling activities during these drilling events are described in Sections 3.1 to 3.3. The analytical results for VOC concentrations for all soil sampling events are summarized in Section 3.4.

3.1 Phase 1: Initial DNAPL Source-Zone Investigations

The primary objectives of the Phase 1 investigation were to determine whether DNAPL was present at Site 88, and to provide a preliminary evaluation of the site hydrostratigraphy. After confirming the presence of DNAPL at the site, a secondary objective of Phase 1 was to characterize the hydraulic properties of the DNAPL zone.

During July 24-28, 1997, 11 soil borings (IS-01 to IS-11) were advanced through the shallow, unconfined aquifer to a maximum depth of 21 ft bgs. Soil boring locations are shown in Figure 3.1. Of the 11 borings, seven were located outside Building 25 near the north wall of the building, two were located inside Building 25 (IS-05 and IS-09), and two were located outside of the south facing wall of the building (IS-04 and IS-06). The borings were sampled continuously with a Geoprobe direct-push rig and the soil core was screened throughout with a photoionization detector (PID) meter to obtain a relative measure of VOC contamination with depth. Soil samples were collected from the core at discrete depth intervals that showed high PID readings.

3.1.1 Soil Sampling Method for VOC Analysis

Soil core retrieved from each borehole with the Geoprobe sampler was contained inside clear acetate core-tube liners to reduce volatile losses of VOCs during the sampling and logging process. Both ends of the core-tube liner were plugged immediately upon retrieval from the borehole to minimize volatilization. The sample tube was then labeled according to sample depth, and small holes were drilled through the core-tube liner at

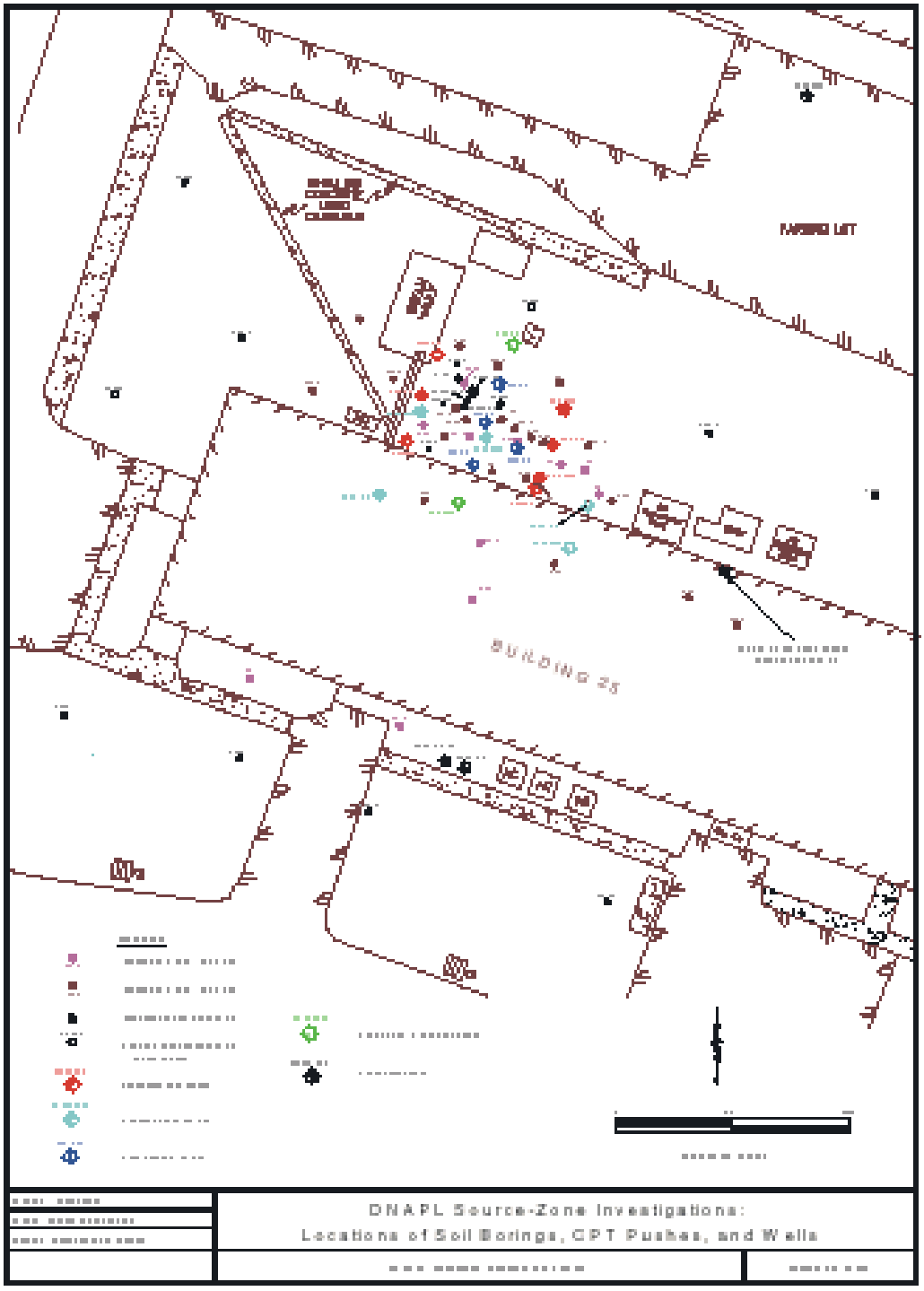

Figure 3.1. DNAPL Source-Zone Investigation: Locations of Soil Borings, CPT Pushes, and Wells

six-inch intervals to allow for PID screening of the soil-filled sample tube. Once the PID screening was completed, discrete soil samples were selected for VOC analysis at intervals that indicated the greatest VOC contamination (i.e., highest PID readings). The discrete soil samples were preserved in the field with methanol, which served the dual purpose of (1) minimizing volatile losses of VOCs from the soil samples during sampling and shipping, and (2) extracting VOCs from the soil sample for laboratory analysis. Soil samples were placed into 40-mL sample vials, which contained a preweighed amount of methanol preservative. After adding the soil sample to the methanol-prepared sample vial, the total weight (i.e., soil plus methanol) was recorded to determine the weight of the collected soil sample. The sampling procedure is can be found in Appendix A.

A new core-tube liner was used for each soil sampling push. All other equipment used in the sampling procedure was properly decontaminated before reuse to minimize cross contamination of samples. The decontamination procedure involved washing sampling tools with Alconox, rinsing with potable water, and allowing them to air dry.

All field samples were catalogued in a sample control log that identified each sample collected, date and time of collection, name of the sampler, and the sample's field identification. Samples were shipped off site to a Quanterra Lab for analysis. For shipment to the lab, samples were packed in a cooler chest with ice, and shipped under chain-of-custody.

3.1.2 Results of Initial DNAPL Source-Zone Investigations

DNAPL was confirmed to be present in the subsurface and was found near the north-facing wall of Building 25 at a depth of approximately 16-20 ft bgs. DNAPL migration was limited vertically by the presence of a clay aquitard that typically begins at about 19 ft bgs. Further details of the Phase 1 investigation, including sampling methods, geologic logs, and laboratory analytical results, are included in the DNAPL Investigation Summary Report (Baker, 1997). The Phase 1 geologic logs are also included in Appendix B of this report.

It should be noted that the analytical lab values for soil VOC concentrations that were reported in the DNAPL Investigation Summary Report (Baker, 1997), as well as in the PITT Work Plan (DE&S, 1998a), for Phase 1 soil samples are in error. The mis-reported soil VOC concentrations by the analytical lab did not include consideration for soil water within the total volume of liquid extracted from the soil samples when analyzed. Further discussion of the cause of the error and the corrected soil VOC concentrations are presented in Section 3.3.1 and Appendix F, respectively, of this report. In addition to confirming the presence of DNAPL at Site 88, the Phase 1 investigation also revealed the presence of light non-aqueous phase liquid (LNAPL) contamination at a depth of approximately 7 - 9 ft bgs, which coincides with the depth of the annual variation of the water table. Since LNAPLs are less dense than water, they

accumulate at the water table (in contrast with DNAPLs, which are denser than water). The depth at which LNAPL contamination occurs at Site 88 exhibits the classic behavior of an LNAPL that becomes smeared across the water-table zone as ground-water levels rise and fall due to seasonal variations in recharge and discharge of the ground-water flow system. During the Phase 1 investigation, it was surmised that the source of the LNAPL was Varsol™ that had leaked from USTs formerly located nearby. As the water table rises and falls with the floating free-phase LNAPL, a portion of the LNAPL becomes trapped by capillary forces in the pore spaces as residual LNAPL.

As a result of the discovery of Varsol™ contamination, a follow-up investigation was conducted at Site 88 by Baker, as discussed in Section 3.2.2 of this report. The results are found in the Varsol™ Investigation Summary Report (Baker, 1998b).

3.1.3 Expanded DNAPL Source-Zone Investigation and Aquifer Testing

After confirming the presence of DNAPL at Site 88 during the initial DNAPL investigation, the Phase 1 investigation was expanded with the following objectives: (1) further delineate the DNAPL zone; (2) characterize the ground-water chemistry of the DNAPL zone; and (3) estimate the hydraulic conductivity of the DNAPL-contaminated shallow aquifer by means of a pumping test. Fieldwork to satisfy these objectives was completed during August 1997.

3.1.3.1 Additional DNAPL Source-Zone Investigation

Five soil borings were completed with continuous sampling to approximately 20 ft bgs. Soil samples were field screened with a PID meter and collected with methanol preservation as described above in Section 3.1.1. Three of the five borings were completed as wells with a hollow-stem auger drilling rig. These three wells were installed for the purpose of aquifer testing. Two of the wells, RW01 and RW02 were screened from 14-19 ft bgs, and well IW01 was screened from 13-18 ft bgs. Wells RW01 and RW02, which were screened to the top of the clay aquitard, revealed the presence of free-phase DNAPL. The depth to free-phase DNAPL (i.e., depth to the interface between ground water and DNAPL pooled in a well) at these two locations was approximately 18-18.5 ft bgs. Ground-water samples were collected from wells RW01 and RW02 for VOC and major ion analysis.

Geologic logs for the borings (IS-12, IS-13, RW01, RW02, and IW01) are included in Appendix B, and well construction details are tabulated in Table 3.1. Soil VOC concentrations and the results of the ground-water analyses are presented in Section 3.3. The aquifer pumping test is discussed below in Section 3.1.3.2. Additional details for this portion of the investigation are included in the Phase 2 section of the DNAPL Investigation Summary Report (Baker, 1997)

Table 3.1 Well Construction Details

Well ID	Casing Diameter (in)	Elevation (ft amsl)		Well Depth (ft bgs)	Screen Intervals (ft amsl)		Bentonite Seal Interval (ft amsl)	Sand Pack Interval (ft amsl)
		Ground	TOC		Lower	Upper		
EX01	4	25.63	25.59	19.96	6.1-10.6	NA	16.8-12.8	12.8-5.6
EX02	4	25.56	25.66	21.20	4.9-9.5	NA	14.7-11.8	11.8-4.2
EX03	4	25.64	25.98	19.94	6.5-11.0	NA	15.9-12.9	12.9-6.0
EX04	4	25.65	25.59	21.09	4.9-9.5	NA	14.1-11.8	11.8-4.6
EX04R	4	25.65	25.59	19.70	6.3-10.9	NA	16.9-13.1	13.1-5.6
EX05	4	25.22	25.42	21.75	4.1-8.7	NA	13.9-11.2	11.2-4.4
EX06	4	25.45	25.73	20.41	5.7-10.3	NA	15.5-12.5	12.5-5.2
HC01	2	26.42	26.85	22.71	4.5-9.1	5.9-15	13.9-11.9	11.9-4.9
HC02	2	25.87	26.17	20.40	6.1-10.8	13.9-18.4	12.8-11.8	11.8-6.1
IN01	4	25.71	25.54	22.58	3.5-8.0	14.0-18.0	12.1-10.1	10.1-3.0
IN02	4	25.27	25.52	19.65	6.5-11.0	14.5-18.5	12.6-11.6	11.6-5.5
IN03	4	25.34	25.8	19.96	6.4-10.9	14.4-18.4	12.9-11.9	11.9-5.8
RW01	4	25.49	25.24	20.00	6.2-10.4	NA	16.2-13.2	13.2-5.2
RW02	4	25.54	25.35	20.00	6.4-10.9	NA	16.4-13.4	13.4-5.4
RW03	2	26.49	26.84	21.97	5.2-9.9	15.8-19.7	14.0-12.0	12.0-5.0
RW04	4	25.78	26.07	23.39	3.3-7.8	13.7-18.2	13.2-11.2	11.2-4.1
RW06	2	26.46	26.86	21.07	6.1-10.8	14.2-18.7	13.9-12.4	12.4-6.4
IW01	2	25.61	25.24	18.50	6.9-11.4	NA	20.7-17.7	17.7-6.2
MW10IW	¼" tube	25.8*	25.0*	39.00	-12.9 - -8.4	NA	8.2-6.1	-6.1-13.34
WP01AQT	¼" tube	25.6*	NA	23.0	2.6-3.6	NA	10.6-4.0	4.0-2.2
WP02AQT	2	25.6*	NA	25.0	0.6-1.6	NA	10.6-2.6	2.6-0.2

*Estimated from nearby wells

3.1.3.2 Aquifer Testing of the DNAPL-Contaminated Zone

A short-term, constant-rate pumping test was conducted on August 22, 1997 to provide preliminary estimates for hydraulic conductivity as well as specific yield. The pumping test configuration, as shown in Figure 3.2, utilized well RW02 as the pumping well, and wells RW01 and TW02 as observation wells. Water levels were monitored at the observation wells by means of an electronic data acquisition system (DAS) with submersible pressure transducers, and were checked manually with the use of an interface probe. The pressure transducers and the interface probe both provided water level measurements recorded in increments of 0.01 feet. Ground water was extracted at well RW02 by means of a variable-speed electric submersible pump. Flow rates were measured by periodically checking the time required for the pumped ground water to fill a calibrated bucket. The pumping test effluent was captured in a tanker and transported to an air stripper on base for treatment by OHM.

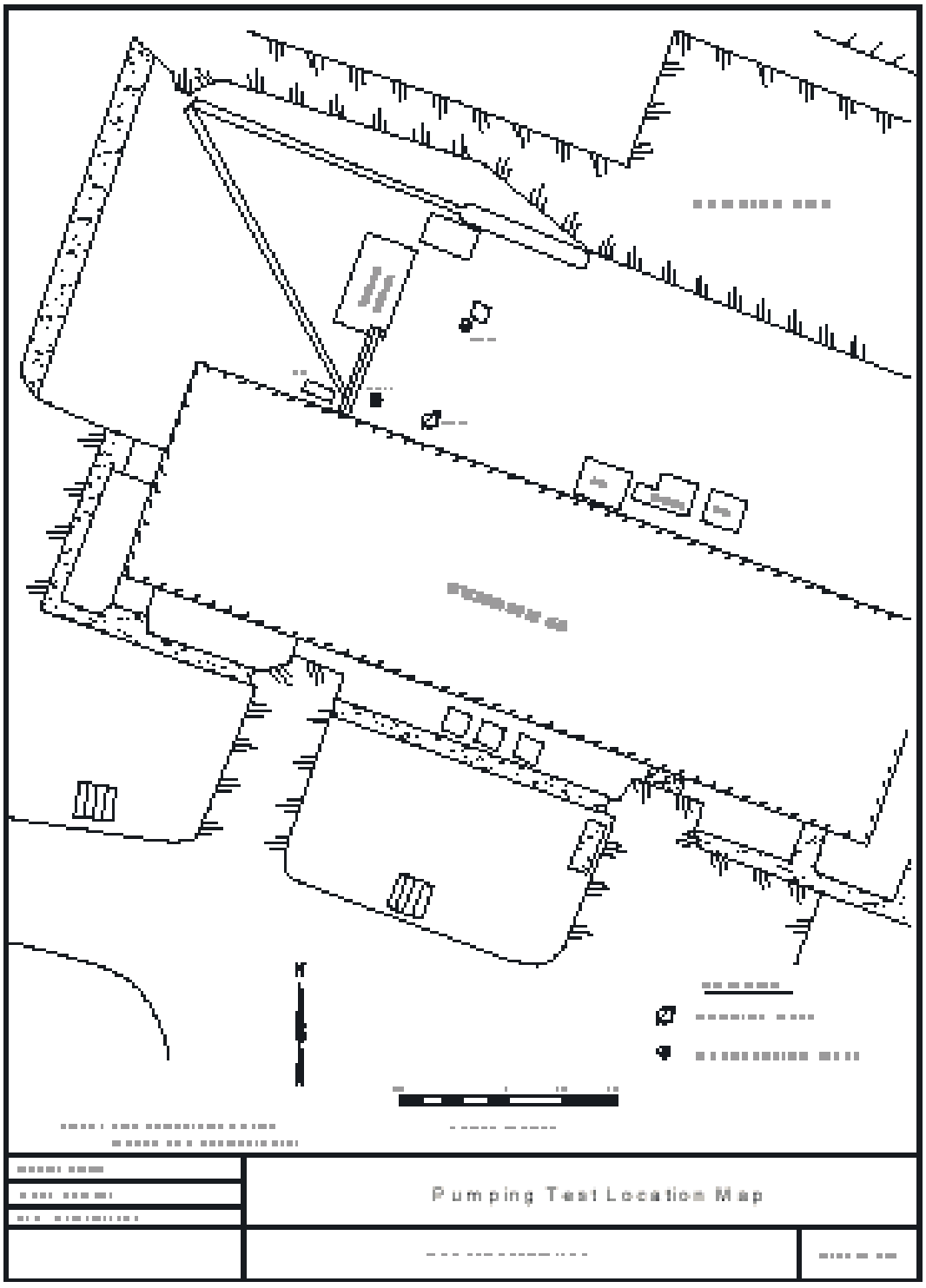

Figure 3.2. Pumping Test Location Map

The pumping test was conducted from noon to 7pm with a constant pumping rate of 0.5 gpm. Data analysis of the water level drawdown at wells RW01 and TW02, using the program AQTESOLV^{TM} and the Neuman method (1975), reveals average values of 5×10^{-4} cm/sec for the hydraulic conductivity and 0.01 for the specific yield. Plots of the drawdown data and curve fits as well as the water level data are included in Appendix C.

The averaged results above for aquifer hydraulic properties were used to develop the geosystem model. The estimated values were later confirmed by the model's ability to accurately predict the results of the CITT and PITT. Although the values given above are representative of the majority of the shallow aquifer in the demonstration area, field observation of core samples indicated that the aquifer sediments become significantly finer (e.g. clayey silt) in the bottom 1-1.5 ft of the aquifer directly overlying the aquitard. This observation of expectedly lower hydraulic conductivity at the base of the shallow aquifer was confirmed by analysis of data from the PITT. Samples collected during the PITT from multilevel sampler points installed in this zone show it to be lower in hydraulic conductivity by a factor of approximately four, as discussed in Section 5.0.

3.2 Phase 2: DNAPL Source-Zone Characterization

Results of the Phase 1 DNAPL source-zone investigation showed that Site 88 was a good candidate for the ESTCP SEAR project. A DNAPL zone had been located and aquifer permeability was found to be sufficient for implementation of the SEAR technology. A Phase 2 DNAPL zone investigation was then conducted to delineate the horizontal extent of DNAPL contamination at Site 88, and to further characterize the clay aquitard. Because DNAPLs are denser and less viscous than water, they tend to migrate downward past the water table until encountering a capillary barrier, such as a clay layer. Consequently, it was important to map the upper surface and thickness of the clay aquitard in the vicinity of the DNAPL zone.

3.2.1 Cone Penetrometer Tests

Cone penetrometer tests (CPTs) were conducted at 12 locations around the periphery of Building 25 to map the upper and lower surfaces of the clay aquitard. Cone penetrometry is a direct-push technology that can be used to provide low cost, rapid characterization of soil types (e.g. sand, silt, clay) versus depth. Different soil types can be inferred by CPT, based upon the inherent properties of a given soil and the forces exerted on the cone-tipped rod as it is pushed downward through the soil column. The method consists of a metal rod equipped with a cone-shaped tip that is pushed downward into the subsurface at a constant rate. A pressure transducer measures and records the pressure exerted on the cone (i.e., tip pressure) which occurs as a function of the physical resistance of the soil to the cone-tipped rod as it is pushed downward through the sediments. At the same time, the sleeve resistance exerted on the drive

rod just above the tip is also measured. For example, pushing a cone-tipped rod through sand creates a greater tip pressure than pushing through clay, whereas the sleeve resistance on the rod as it is pushed downward is greater for clay than sand due to the shear forces exerted by the clay. The combined data logs of tip pressure and sleeve resistance are used to generate a soil column log to characterize soil type versus depth.

CPT push locations are shown in Figure 3.1. Of the 12 CPT pushes, six were terminated after about two feet of penetration into the clay layer. These shallow CPT pushes provided the necessary data to map the upper surface of the clay layer, yet prevented downward DNAPL migration through the aquitard since the push did not penetrate the full thickness of the aquitard (CPT02, 03, 05, 07, 09, and 12). At six locations known to be outside the DNAPL zone, CPT pushes were advanced completely through the clay aquitard until encountering sand below the aquitard, in order to map the approximate thickness of the shallow clay layer (i.e., capillary barrier) around Building 25 (CPT01, 04, 06, 08, 10, and 11).

CPT logs are included in Appendix D. Results of the CPT investigation indicate that the clay layer varies in thickness from about 8-14 ft thick on the north side of Building 25. On the south side of the building, clay thickness generally ranges from about 2-10 ft, but thins to only about four inches at CPT08 which is located near the southwest corner of the building.

After each CPT push, the rig moved approximately one foot, and then repeated the push to collect discrete, one-foot soil core samples from two depth intervals, as directed by the DE&S geologist on site. Soil samples were collected in one-inch ID X 12-inch long acetate core liners at a depth interval of 8-9 ft bgs for Varsol™ analysis, and also from just above the clay interface for DNAPL analysis. Varsol™ concentrations in the CPT soil samples are included in the Varsol™ Investigation Summary Report (Baker, 1998b), and VOC concentrations in the CPT soil samples are discussed in Section 3.4 of this report.

3.2.2 Soil Borings to Delineate Extent of DNAPL Zone

During November 1997, 18 soil borings (IS-14 to IS-31) were completed at Site 88 to delineate the horizontal extent of the DNAPL zone at Building 25. The total depth of the soil borings ranged from 20-22 ft bgs, and the borings were generally terminated after penetrating the clay layer by about one to two feet. Soil sampling was conducted with a Geoprobe direct push macrosampler tube. Continuous soil sampling was completed from ground surface to the clay aquitard for borings IS-14 and IS-15, whereas at the remaining borings (IS-16 to IS-31) core samples were collected only at discrete depth intervals, from 8-10 ft bgs for Varsol™ analysis and from ~16-21 ft bgs for VOC analysis. All core samples were field screened with a PID, and VOC soil samples were field-preserved with methanol, as described in Section 3.1.1. Soil cores were described

according to soil type. The geologic logs are included in Appendix B. Soil boring locations for IS-14 to IS-31 are shown in Figure 3.1. Soil VOC concentrations are presented in Section 3.4

The purpose of the Varsol™ investigation was twofold – first, to investigate the presence of LNAPL Varsol™ which could potentially affect the SEAR process, and second, to provide baseline information for the remediation of Varsol™ contamination. The details and results of this investigation are found in the Varsol™ Investigation Summary Report (Baker, 1998b). Varsol™ was reported as high as 4,900 mg/kg in soil samples and 7,100 µg/L in ground-water samples. Free-phase Varsol™ has not been observed in any wells on site.

Fourteen of the soil borings during this investigation were located on the north side of Building 25, and four borings were located inside the building. Boring locations were chosen based on data gaps from the previous soil sampling events so that the approximate horizontal extent of the DNAPL zone could be mapped as a result of this soil sampling event. Soil samples were also collected from four soil borings located in an area already known to contain DNAPL. The purpose of collecting soil samples from these four borings was to provide pre-SEAR data that would allow a performance assessment (PA) of the effectiveness of the surfactant flood. The four PA borings are IS-22, IS-23, IS-25, and IS-26. Baseline DNAPL conditions for the four borings were determined by collecting soil samples from three discrete depths near the bottom of each boring. After the surfactant flood is completed, soil samples will be collected at the same depths near these borings for VOC analysis. The post-SEAR soil VOC concentrations will then be compared to soil VOC concentrations for the pre-SEAR soil samples.

A second objective for this Phase 2 round of soil sampling was to provide further characterization of the DNAPL-zone geosystem, including: (1) improved mapping of the depth to the upper surface of the clay layer; (2) analysis of soil samples to determine mineral content; and (3) analysis of the fraction of sedimentary organic carbon (f_{oc}) in soil samples. The results of mineral and f_{oc} analyses are presented in Section 3.3.1. Mapping of the upper surface and thickness contours of the clay layer is discussed in Section 5.0.

3.2.3 Soil Sampling during Installation of Test Zone Wells

The test zone wells and associated recovery wells were installed on the north side of Building 25 during December 1997, and included three wells that were installed inside the building. Soil samples were collected from the DNAPL zone at the well locations to measure the pre-SEAR DNAPL saturations in the test zone. Soil sampling intervals from soil borings at the well locations are discussed here, and well installation methods are discussed in Section 4.0.

Soil borings were drilled at each well location and core samples were collected continuously, typically from about 16-21 ft bgs. Soil samples were collected by split spoon sampling from the borings at EX01, EX02, EX03, RW03, RW06 and HC01, whereas the remaining borings, EX04, EX05, EX0, IN01, IN02, and IN03, were sampled continuously with a Geoprobe macrosampler. Core sampling depth intervals, PID readings and descriptions of the soil types were recorded on a geologic log for each well location. The geologic logs are included in Appendix B.

Soil cores were field screened immediately upon retrieval with a PID meter to obtain a relative measure of VOC contamination with depth. The specific objective of this PID screening was to locate the interface where PID readings became non-detectable or decreased to near zero. This provided an indication of the extent of VOC contamination with depth, which coincided with the upper portion of the clay layer. Once the zero-VOC/clay-layer interface was located, three discrete soil samples were collected from each borehole for VOC analysis; one sample was collected at six inches above the interface, one at 1.5 feet above the interface and one at three feet above the interface. Each soil sample was collected into a jar and preserved in the field with methanol, as described in Section 3.1.1.

3.3 Soil and Water Analysis

The analytical results from soil and ground-water samples collected during the DNAPL source-zone investigations are presented in this section of the report. The analytical chemistry data is used to build a geosystem model of the site for the purposes of characterizing the DNAPL zone and to provide the necessary input for designing a PITT and surfactant flood (as part of SEAR). The geosystem of the test zone at Site 88 is described in Section 5.0. The raw analytical data (e.g., soil VOC concentrations, soil moisture content, and f_{oc}) are used to estimate the percent DNAPL saturation (S_n) for each soil sample collected in the DNAPL zone, as discussed in Section 3.3.1. Soil samples were also collected for analysis by X-ray diffraction (XRD) to determine the mineral composition of sediments in the DNAPL zone.

Ground-water and source-water (i.e., site potable water) samples were also analyzed to characterize VOC and major-ion concentrations in the DNAPL zone ground water and source water. The ionic composition of the ground water and source water must be determined for PITT and SEAR design purposes. Site source water will be used to mix tracer and surfactant injectate solutions.

3.3.1 Soil Analysis

Soil samples collected during the DNAPL investigations and well installations were shipped to Quanterra Inc., in Knoxville, Tennessee and analyzed for VOCs to evaluate the spatial distribution of the PCE, TCE, and DCE contamination in the subsurface. For

a given soil sample, the reported concentration represents the bulk VOC concentration in a wet soil sample, which is the sum of VOCs associated with four phases: air (if in the vadose zone), water, soil, and nonaqueous phase liquid (NAPL). The bulk soil VOC concentration data reported by the lab were analyzed using NAPLANAL, a computer code developed by DE&S (Mariner et. al., 1997). The program estimates the aqueous VOC concentrations originally present in the wet soil samples and determines if any NAPL is present. NAPLANAL calculates the distribution of the measured total soil VOC concentrations from a bulk sample to the various VOC phases: fluid (i.e., water and air), solid (i.e., sorption to soil), and NAPL. Partitioning of VOCs between the air, water, soil, and NAPL phases depends upon well-established partition coefficients and solubility constants. If the calculations indicate that aqueous concentrations exceed the solubility and sorption constraints, then the NAPLANAL algorithm estimates the NAPL saturation. The NAPLANAL output includes the calculated VOC concentration in each phase and the NAPL saturation. If there is no NAPL present, a dilution factor can be calculated to provide a measure of how dilute the sample is with respect to the aqueous solubility of the VOC.

In addition to the soil VOC analyses, soil samples were also collected to determine the f_{oc} and soil moisture content. These parameters are needed to conduct the NAPLANAL calculations. Three samples were analyzed for f_{oc} by AnalySys, Inc., of Austin, Texas. The f_{oc} analyses were performed using EPA method ASA 29-3.5.2. This method measures non-purgeable organic carbon and includes a special pretreatment procedure to remove inorganic carbon (i.e., carbonate minerals) that could interfere with the f_{oc} measurement. The method requires the sample to be dried before analysis to remove water and purgeable organic carbon (i.e., VOCs). Traditional f_{oc} analyses have potential interferences that cannot be tracked, and which tend to overestimate the f_{oc} measurements (Caughey et al., 1995). The results of the f_{oc} analyses are shown in Table 3.2. The measured f_{oc} in the DNAPL zone ranges from 1510 to 6420 mg/kg and increases with depth and increasing fineness of the aquifer sediments. These values are equivalent to 0.00151 and 0.00642, respectively, when represented as the fraction of organic carbon relative to the bulk soil mass. A significant difference in f_{oc} was noted between the sandy versus clayey sediments, which is consistent with the geologic logs that indicate increasing peat content with depth in the clayey sediments. The analytical results can be found in Appendix E.

Table 3.2 Fraction of Organic Carbon (f_{oc}) in Selected Soil Samples

Sample ID	Depth (ft bgs)	Texture	f_{oc} (mg/kg)
IS26-04	16.5	Fine sand	1510
IS26-05	18.0	Clayey silt	5560
IS26-06	19.0	Silty clay	6420

Soil moisture, or water content, was determined for five soil samples collected at various boring locations and depths. The analysis was performed by Quanterra Inc., Knoxville, Tennessee using method MCAWW 160.3 MOD. The water content was in the range of 17.3 % to 21.2% (by weight). The results are given in Table 3.3. The laboratory data is in Appendix E.

Table 3.3 Soil Water Content

Sample ID	Depth (ft bgs)	Texture	Water Content (% by weight)
IW01-04	4.2	Clayey fine sand	17.3
IW01-05	9.2	Fine sand	17.5
IW01-09	18.2	Silty clay	20.2
RW02-04	9.2	Fine sand	18.1
IS13-08	18.2	Fine sand	21.2

Soil VOC concentrations are listed in Table 3.4 for all samples collected during the DNAPL source-zone investigations described in Sections 3.1 to 3.3. Percent NAPL saturation is also shown in Table 3.4, which is discussed in Section 3.4.2.

As mentioned previously in Section 3.1.2, the soil VOC values shown in Table 3.4 have been corrected from the earlier erroneous values reported by the lab and summarized in the initial DNAPL Investigation Summary Report (Baker, 1997) and in the PITT Work Plan (DE&S, 1998a). The erroneous values, based upon VOC concentrations in the methanol preservative/extraction solvent, did not include soil water content in the conversion calculation performed to estimate soil VOC concentrations. The corrections, however, reflect the addition of soil water content to the conversion calculation. A detailed description of the correction calculation process and a sample calculation are provided in Appendix F. Laboratory reports of the soil core VOC analyses can be found in Appendix H.

3.3.2 NAPLANAL Estimates of DNAPL Saturations

The corrected soil VOC concentrations shown in Table 3.4 were used as input to the NAPLANAL program to estimate the percent DNAPL saturation, i.e., the percentage of pore space that is occupied with DNAPL, for each soil sample. The calculated DNAPL saturation is a function of the porosity (i.e., volume of pore space per unit volume of soil) and the f_{oc} (i.e., related to adsorption potential) of the soil matrix. Porosity was calculated based upon measured water content from soil samples collected during the DNAPL source-zone investigations. A soil water content of 20% was used for the porosity calculation, which implies a porosity of 0.40. This value is consistent with reported values of porosity for fine sand and silt (Freeze and Cherry, 1979), and is considered representative for the soil samples collected at Site 88. The porosity calculation is included in Appendix G.

Table 3.4 Soil VOC Concentrations of Subsurface Soils at Building 25

Sample ID	Sample Date	Depth (ft bgs)	Soil Concentration (mg/kg)			f_{oc}	Calculated % NAPL Saturation
			PCE	TCE	DCE		
IR88-IS01-1	7/25/97	5.3	ND	ND	19	0.0015	0.0
IR88-IS01-2	7/25/97	8.1	72.8	6.9	43.3	0.0015	0.0
IR88-IS01-3	7/25/97	8.6	101.4	38.6	49.9	0.0015	0.0
IR88-IS01-4	7/25/97	10.1	114.0	8.4	35.1	0.0015	0.0
IR88-IS02-1	7/25/97	8.1	13.1	2.1	15.1	0.0015	0.0
IR88-IS02-2	7/25/97	8.6	0.7	3.0	3.2	0.0015	0.0
IR88-IS02-3	7/25/97	8.9	64.8	ND	49.5	0.0015	0.0
IR88-IS02-4	7/25/97	16.3	0.1	ND	ND	0.0015	0.0
IR88-IS03-1	7/25/97	2.6	16.9	0.5	ND	0.0015	0.0
IR88-IS03-2	7/25/97	5.9	1.2	ND	ND	0.0015	0.0
IR88-IS03-3	7/25/97	7.6	7.2	ND	0.2	0.0015	0.0
IR88-IS04-1	7/26/97	12.1	7.3	ND	ND	0.0015	0.0
IR88-IS05-1	7/26/97	2.6	209	ND	ND	0.0015	0.02
IR88-IS05-2	7/26/97	5.7	653	ND	ND	0.0015	0.2
IR88-IS05-3	7/26/97	8.2	3,508	ND	ND	0.0015	1.0
IR88-IS05-4	7/26/97	10.3	372	25.4	ND	0.0015	0.1
IR88-IS06-1	7/26/97	9.2	3.2	ND	ND	0.0015	0.0
IR88-IS07-1	7/26/97	5.1	0.1	ND	3.6	0.0015	0.0
IR88-IS07-2	7/26/97	8.6	195	6.9	81.5	0.0015	.02
IR88-IS07-3	7/26/97	11.0	58.0	4.0	32.6	0.0015	0.0
IR88-IS07-4	7/26/97	18.4	1,901	ND	ND	0.0060	0.4
IR88-IS08-1	7/27/97	17.6	13,748	ND	ND	0.0015	4.2
IR88-IS08-2	7/27/97	18.7	5,997	ND	ND	0.0060	1.7
IR88-IS08-3	7/27/97	19.4	2,617	ND	ND	0.0060	0.7
IR88-IS08-4	7/27/97	4.7	1,268	133	ND	0.0015	0.4
IR88-IS08-5	7/27/97	7.3	1,577	258	ND	0.0015	0.5
IR88-IS09-1	7/27/97	10.6	188	ND	ND	0.0015	0.01
IR88-IS09-2	7/27/97	14.7	24	ND	ND	0.0015	0.00
IR88-IS10-1	7/27/97	15.4	80	3.7	3.7	0.0015	0.0
IR88-IS10-2	7/27/97	16.2	20	0.6	0.8	0.0015	0.0
IR88-IS10-3	7/27/97	17.2	25,829	ND	ND	0.0015	7.9
IR88-IS010-4	7/27/97	17.7	3,841	ND	ND	0.0060	1.0
IR88-IS11-1	7/27/97	16.4	12,169	ND	ND	0.0060	3.6
IR88-IS12-01	8/19/97	15.6	52	ND	ND	0.0015	0.0
IR88-IS12-02	8/19/97	16.1	22	0.18	ND	0.0060	0.0
IR88-IS12-03	8/19/97	17.1	32	ND	ND	0.0015	0.0
IR88-IS13-01	8/19/97	17.1	7,760	ND	ND	0.0015	2.3
IR88-IS13-02	8/19/97	17.6	25,411	ND	ND	0.0015	7.9
IR88-IS13-03	8/19/97	18.1	6,226	ND	ND	0.0015	1.9

Table 3.4, continued

Sample ID	Sample Date	Depth (ft bgs)	Soil Concentration (mg/kg)			f_{oc}	Calculated % NAPL Saturation
			PCE	TCE	DCE		
IR88-RW01-01	8/19/97	17.1	31	ND	ND	0.0015	0.0
IR88-RW01-02	8/19/97	18.1	11,337	ND	ND	0.0060	3.3
IR88-RW01-03	8/19/97	20.1	1,483	ND	ND	0.0060	0.3
IR88-RW02-01	8/19/97	17.1	16	ND	ND	0.0015	0.0
IR88-RW02-02	8/19/97	18.1	1049	ND	ND	0.0015	0.3
IR88-RW02-03	8/19/97	18.6	4,634	ND	ND	0.0060	1.3
IR88-IW01-01	8/20/97	17.6	138	ND	ND	0.0015	0.0
IR88-IW01-02	8/20/97	18.1	33,572	ND	ND	0.0060	10.2
IR88-IW01-03	8/20/97	18.6	5,140	ND	ND	0.0060	1.4
IR88-IW01-06	8/20/97	4.2	1.7	ND	22	0.0015	0.0
CPT01-2	11/15/97	15.2	ND	ND	ND	NA	0.0
CPT02-2	11/15/97	17.2	ND	ND	ND	NA	0.0
CPT03-2	11/15/97	18.2	32	ND	ND	0.0060	0.0
CPT04-2	11/15/97	18.2	60	ND	ND	0.0060	0.0
CPT05-2	11/15/97	19.5	1.3	0.1	ND	0.0060	0.0
CPT07-2	11/15/97	17.0	3.9	0.3	ND	0.0015	0.0
CPT08-2	11/15/97	21.0	8.0	0.3	ND	0.0060	0.0
CPT09-2	11/15/97	17.6	3.0	ND	ND	0.0015	0.0
CPT10-2	11/15/97	18.4	0.5	ND	ND	0.0015	0.0
IS14-2	11/18/97	18.0	0.05	ND	ND	0.0060	0.0
IS15-2	11/18/97	19.0	3.4	0.05	ND	0.0015	0.0
IS16-2	11/19/97	18.5	3,261	ND	ND	0.0060	0.9
IS17-2	11/19/97	18.0	5,930	ND	ND	0.0015	1.8
IS18-2	11/19/97	18.4	5.4	.1	ND	0.0060	0.0
IS19-2	11/19/97	17.4	0.1	ND	ND	0.0015	0.0
IS20-2	11/19/97	18.5	2.9	ND	ND	0.0015	0.0
IS21-3	11/20/97	19.7	908	ND	ND	0.0015	0.2
IS21-4	11/20/97	18.7	8763	ND	ND	0.0015	2.6
IS22-2	11/20/97	17.0	3,603	ND	ND	0.0015	1.1
IS22-3	11/20/97	18.0	2,815	ND	ND	0.0015	0.8
IS22-4	11/20/97	19.0	909	ND	ND	0.0060	0.1
IS23-1	11/20/97	17.5	9.3	ND	ND	0.0015	0.0
IS23-2	11/20/97	18.2	1,476	ND	ND	0.0015	0.4
IS23-3	11/20/97	19.0	311	ND	ND	0.0060	0.0
IS25-2	11/21/97	17.0	1,709	ND	ND	0.0015	0.5
IS25-3	11/21/97	18.0	10,851	ND	ND	0.0060	3.2
IS25-4	11/21/97	19.0	814	ND	ND	0.0060	0.1
IS26-1	11/21/97	17.0	208	ND	ND	0.0060	0.0
IS26-2	11/21/97	17.7	1,611	ND	ND	0.0060	0.4

Table 3.4, continued

Sample ID	Sample Date	Depth (ft bgs)	Soil Concentration (mg/kg)			f_{oc}	Calculated % NAPL Saturation
			PCE	TCE	DCE		
IS26-3	11/21/97	18.5	106	ND	ND	0.0060	0.0
IS29-2	11/22/97	18.8	4,361	ND	ND	0.0060	1.2
IS30-2	11/22/97	18.8	3,212	ND	ND	0.0060	0.8
IS31-2	11/22/97	16.8	54	ND	ND	0.0060	0.0
EX01-1	12/3/97	16.5	3,013	ND	ND	0.0015	0.9
EX01-2	12/3/97	17.5	44,352	ND	ND	0.0015	13.7
EX01-3	12/3/97	18.5	29,763	ND	ND	0.0015	9.1
EX03-1	12/4/97	16.0	1.2	ND	ND	0.0015	0.0
EX03-2	12/4/97	17.5	19	ND	ND	0.0015	0.0
EX03-3	12/4/97	19.0	96	ND	ND	0.0015	0.0
EX04-1	12/4/97	17.0	122	1.8	2.2	0.0015	0.0
EX04-2	12/4/97	18.5	25	ND	ND	0.0015	0.0
EX04-3	12/4/97	19.5	11,743	ND	ND	0.0015	3.6
EX05-1	12/4/97	18.0	2.3	ND	0.4	0.0015	0.0
EX05-2	12/4/97	19.0	0.8	ND	3.1	0.0015	0.0
EX05-3	12/4/97	20.0	86	ND	ND	0.0015	0.0
EX06-1	12/5/97	16.5	0.7	ND	0.5	0.0015	0.0
EX06-2	12/5/97	18.0	0.8	ND	ND	0.0015	0.0
EX06-3	12/5/97	19.0	0.5	ND	ND	0.0015	0.0
HC01-1	12/8/97	18.5	1,540	ND	ND	0.0015	0.4
HC01-2	12/8/97	20.0	10,489	ND	ND	0.0015	3.2
HC01-3	12/8/97	21.0	712	ND	ND	0.0060	0.1
IN01-1	12/8/97	18.0	13,406	ND	ND	0.0015	4.1
IN01-2	12/8/97	19.5	15,553	ND	ND	0.0060	4.6
IN01-3	12/8/97	20.5	708	ND	ND	0.0015	0.2
IN03-1	12/8/97	16.0	5.2	0.1	0.6	0.0015	0.0
IN03-2	12/8/97	17.5	2.7	ND	ND	0.0015	0.0
IN03-3	12/8/97	19.0	18	0.2	ND	0.0015	0.0
HC02-1	12/9/97	16.0	1.2	0.1	0.1	0.0015	0.0
HC02-2	12/9/97	17.0	9.4	0.1	ND	0.0015	0.0
HC02-3	12/9/97	18.5	25	0.2	ND	0.0015	0.0
RW03-2	12/9/97	21.6	287	1.7	ND	0.0015	0.04
RW04-1	12/9/97	18.0	25	0.1	ND	0.0015	0.0
RW04-2	12/9/97	19.5	23,057	ND	ND	0.0015	7.1
RW04-3	12/9/97	20.5	448	ND	ND	0.0060	0.0

Notes: PCE = tetrachloroethene
TCE = trichloroethene

DCE = *cis*-1,2-dichloroethene

f_{oc} = fraction of sedimentary organic carbon
Calculated % NAPL saturation = fraction of the pore space occupied by NAPL calculated using NAPLANAL
ND = compound not detected

Measured f_{oc} in the DNAPL zone was noted to increase with depth from sandy to clayey sediments, as shown in Table 3.2. This is consistent with field observations of soil cores, where peat content was found to be more heavily associated with the clayey sediments, which increases the sedimentary organic carbon content. It should be noted that the peat was observed to be present as peat particles dispersed within the finer-grained sediments, and not as layers or lenses of peat. Two values for f_{oc} were used input into the NAPLANAL calculations; a value of 0.0015 (1,500 mg/kg) was used for samples collected in predominately sandy soils, and a value of 0.006 (6,000 mg/kg) was used for samples collected in silty or clayey soils. Results from the NAPLANAL calculations are presented in Table 3.4, as well as the f_{oc} value used, based on the soil type of the sample, for each NAPLANAL calculation. The algorithm used in NAPLANAL to calculate DNAPL saturations is described fully by Mariner et. al. (1997); a copy of this paper is included in Appendix G.

The analysis indicates that DNAPL is present directly underneath Building 25 and in an area adjacent to the north side of building. The DNAPL saturation is in the range of 0.01 to 13.7%. The approximate horizontal extent of the DNAPL zone is shown in Figure 3.3. The DNAPL-zone boundary line (see Figure 3.3) is based upon measured soil VOC concentrations and the resulting DNAPL saturations calculated by NAPLANAL. Cross sections were constructed to show the soil VOC concentrations and DNAPL saturations at Site 88. The plan view locations of cross-section transects A-A' and B-B' are shown in Figure 3.3. Cross sections A-A' and B-B' are depicted in Figures 3.4 and 3.5. The cross sections provide insight into the vertical distribution of DNAPL in the contaminated zone, which indicates that the DNAPL saturation generally increases with depth from about 16 to 20 ft bgs. DNAPL saturation data in Table 3.4 and in the cross sections in Figures 3.4 and 3.5 show that the horizontal distribution of the DNAPL zone is most concentrated along the north side of Building 25.

3.3.3 Ground-Water and Source-Water Characterization

Ground-water samples collected from wells RW01 and RW02 were shipped to Quanterra Inc., Knoxville, Tennessee for VOC analysis. The results are given in Table 3.5 and reveal that the PCE concentrations are in the range of 150 to 170 mg/L. The laboratory reports can be found in the initial DNAPL Investigation Summary Report (Baker, 1997; App C)

Table 3.5 Ground-Water VOC Concentrations

Well	Sample Date	PCE (mg/L)	TCE (mg/L)	DCE (mg/L)
RW01	8/21/97	170.0	*3.2	11.0
RW02	8/22/97	150.0	*3.5	10.0

*concentration below calibration range.

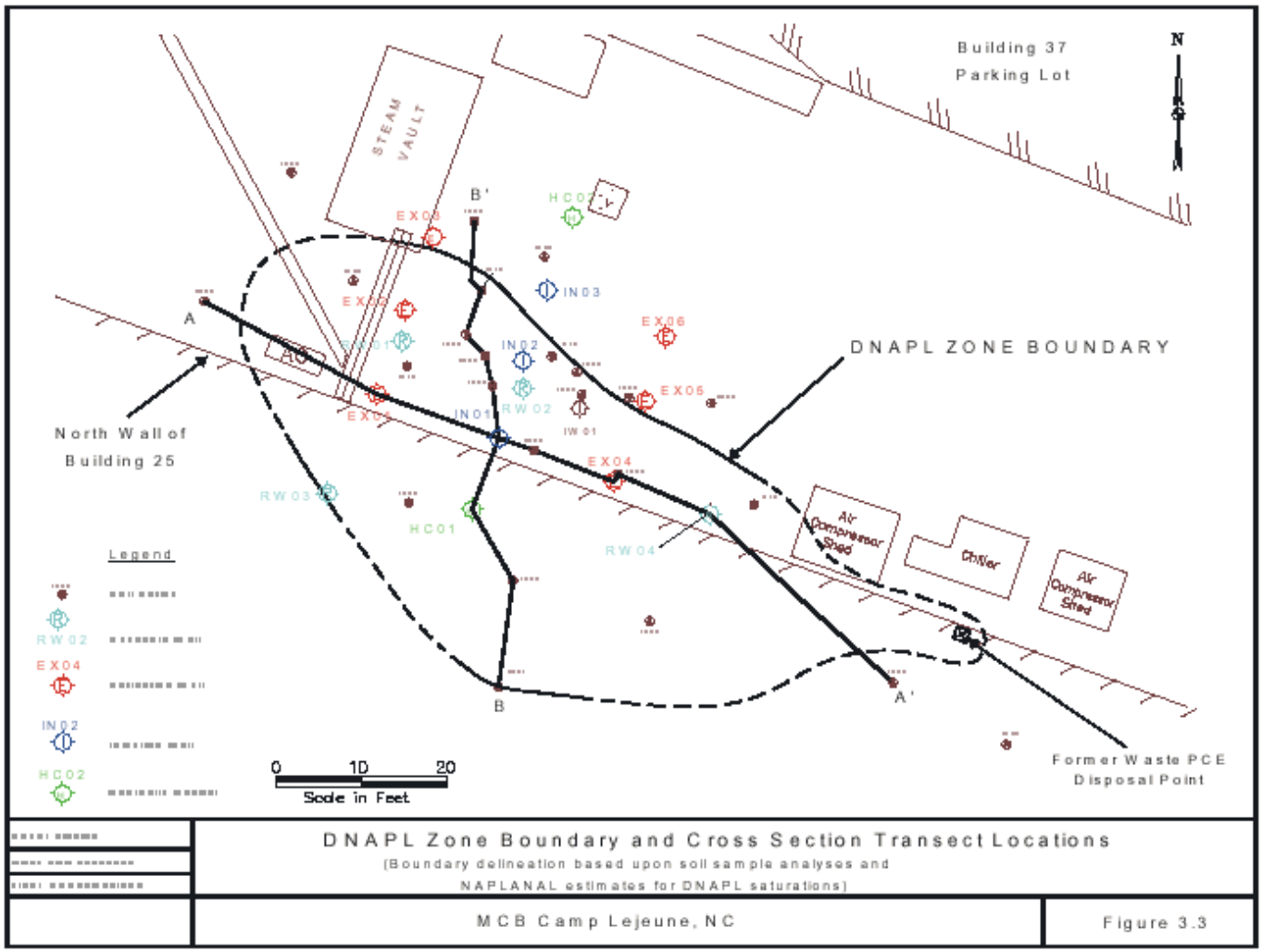

Figure 3.3. DNAPL Zone Boundary and Cross Section Transect Locations

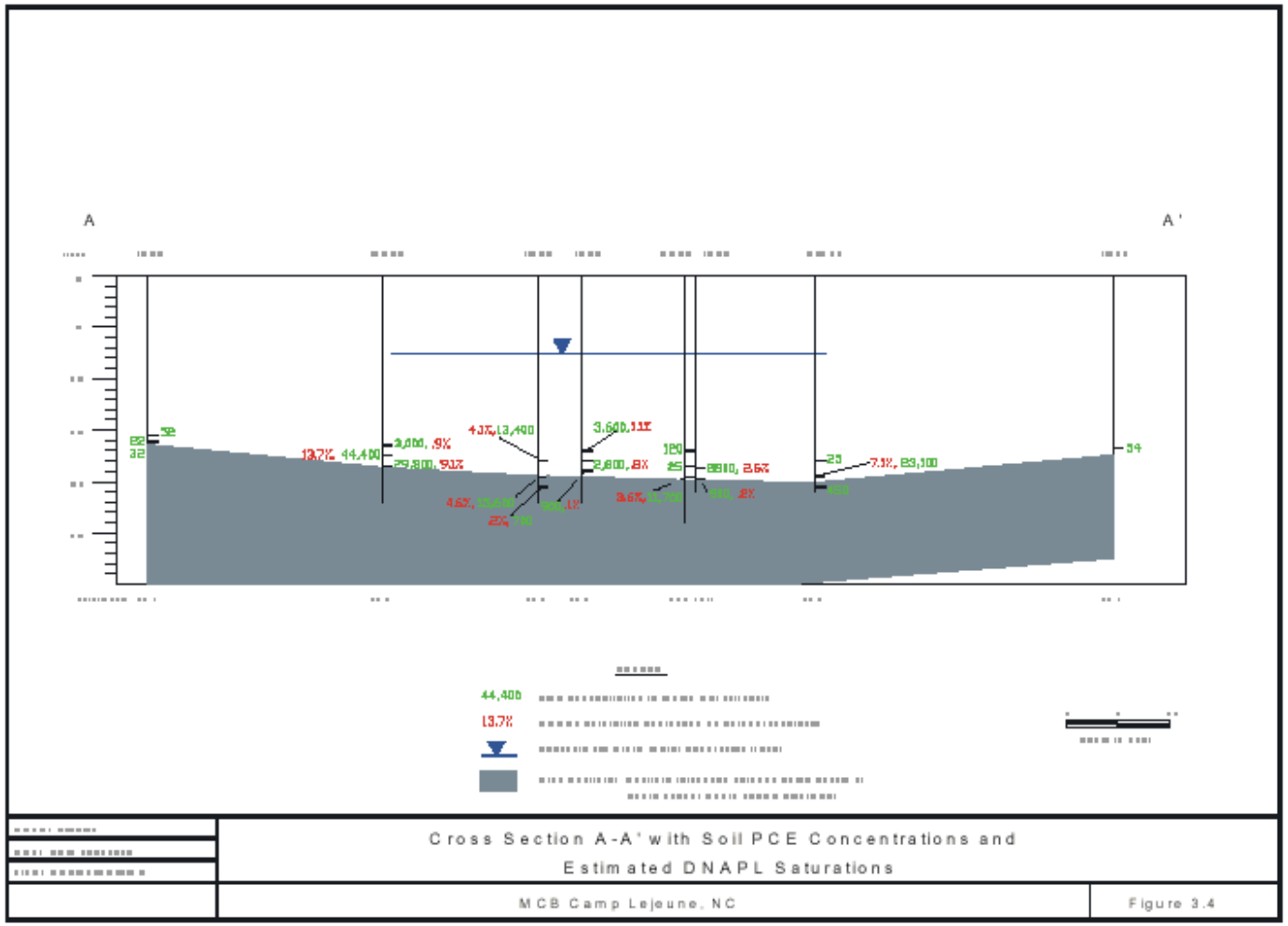

Figure 3.4. Cross Section A-A’ with Soil PCE Concentrations and Estimated DNAPL Saturations

Duke Engineering & Services
A Duke Energy Company

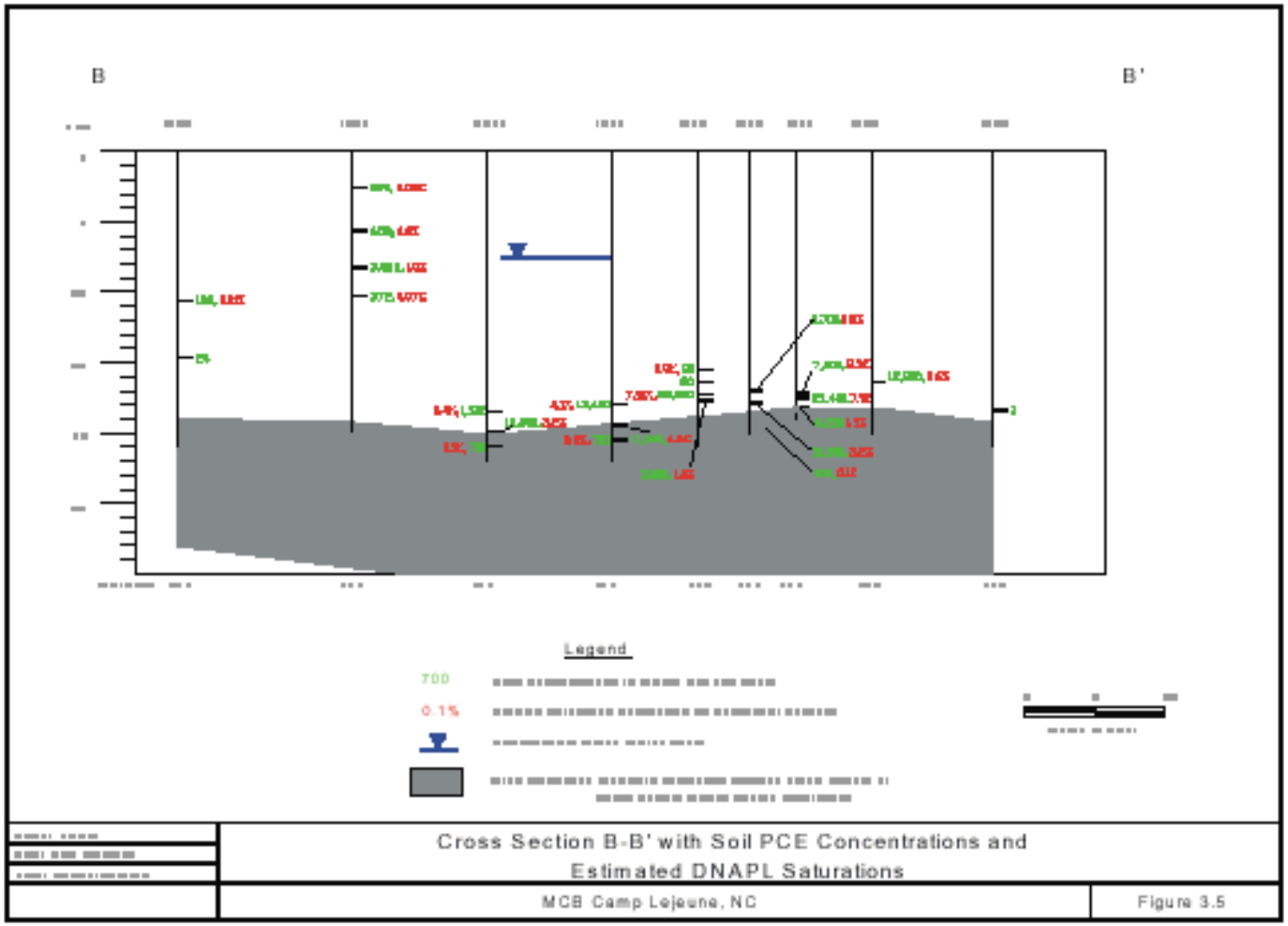

Figure 3.5. Cross Section A-A' with Soil PCE Concentrations and Estimated DNAPL Saturations

Ground-water and source-water samples were collected from Site 88 on November 17, 1997 and were analyzed for major ion composition to characterize both waters for tracer and surfactant design considerations. Ground-water samples collected from wells RW01 and RW02, and a source-water sample collected from a potable water outlet inside Building 25 were shipped to Quanterra Inc., Knoxville, Tennessee for major anion and cation analyses. Major ion concentration data is summarized in Table 3.6. These analyses indicate that the ground water is probably anoxic because of the abundance of dissolved iron.

Table 3.6 Major Ion Concentrations in Ground-Water and Source-Water Samples

ION		Sample location		
		RW01	**RW02**	**Source Water**
Cations (mg/L)	*Aluminum*	0.28	0.33	0.20
	Calcium	15.7	15.1	26.9
	Iron	25.8	6.1	ND
	Potassium	ND	9.9	ND
	Magnesium	ND	5.3	ND
	Manganese	0.094	0.10	ND
	Sodium	19.7	30.9	9.0
	Zinc	0.023	.039	ND
Anions (mg/L)	*Chloride*	66.0	45.5	12.4
	Sulfate	16.1	46.7	5.4
Total Alkalinity (mg/L)		28.2	ND	63.9

ND = non detect

4.0 TEST ZONE WELL-FIELD INSTALLATION

4.1 Test Zone Wells and DNAPL Recovery Wells

The primary objective of this drilling program was to install the well field to be used in the PITT/SEAR demonstration. The goal was to locate the PITT/SEAR injection and extraction wells in the area with the highest known DNAPL saturations on the north side of Building 25. The test zone well-field location was chosen based on analysis of data obtained from reconnaissance soil borings completed during Phases 1 and 2 of the DNAPL source-zone investigations, as discussed in Section 3.0. Several recovery wells were also installed outside the test zone well field to provide a means of removing free-phase DNAPL from areas beyond the test zone wells. Numerical modeling was performed to optimize the well-field configuration (total number of wells and interwell distances), as discussed in Section 8.2.1.

A second objective was to collect soil samples during the well installations to determine DNAPL saturations in sediments collected from the well locations. All boreholes drilled during the well-field installation, along with all other boreholes and monitor points are shown on Figure 3.1. Soil borings at EX01, EX02, EX03, EX04, EX05, and EX06 were completed as extraction wells, and soil borings at IN01, IN02, and IN03 were completed as injection wells. HC01 and HC02 were completed as hydraulic control wells. RW01, RW02, RW03, RW04, and RW06 were completed as recovery wells, the primary purpose of which is to recover free-phase DNAPL, and a secondary purpose for use as monitor wells during the SEAR demonstration. Wells RW01 and RW02, the first two wells installed during the DNAPL investigations, were installed with a two-fold intent: (1) for aquifer testing in the DNAPL zone, and (2) for potential use as PITT wells. The final PITT design, however, precluded the use of RW01 and RW02 as PITT/SEAR wells due to their location. Well EX04R was installed as a replacement well for EX04, which was fouled during installation and not effective as an extraction well. Well MW10IW was installed within the test zone well field, screened in the Upper Portion of the Castle Hayne Aquifer as a monitor well for the surfactant flood. Also, two aquitard monitor points were installed adjacent to MW10IW in the clay layer during the surfactant flood. To summarize, the following well types have been installed at Site 88 that are related to the PITT/SEAR demonstration, and are shown in Figure 3.1:

Test Zone Wells:

- six extraction wells EX01 to EX06
- one replacement extraction well EX04R
- three injection wells IN01 to IN03

- two hydraulic control wells HC01 and HC02

Recovery Wells:

- five DNAPL recovery wells RW01 to RW04, and RW06

Monitor Points/Wells:

- three multilevel samplers MLS-1, MLS-2, and MLS-3
- two aquitard well points WP01AQT and WP02AQT
- one Castle Hayne monitor well MW10IW

4.2 Drilling Methods for Well-Field Installation

All of the well installations outside Building 25 were drilled with a six-inch ID hollow stem auger. Due to overhead limitations for drilling inside the building, wells installed inside Building 25 were drilled using a six-inch steel drive casing, an electric powered 300-pound hammer with telescopic tower, and a hand auger. After coring through the concrete floor inside the building, five-foot lengths of casing were driven into the soil beneath the concrete slab of Building 25. A hand auger was used to excavate the soils from within the casing until the water table was reached. Below the water table, the fine-grained sand and silt was removed from the borehole by injecting potable water into the casing, causing a slurry to spill out of the drive casing at the surface. This slurry was contained in a settling tank adapted to fit around the well casing to allow drill cuttings to settle out from the slurry. Drilling fluids were then transferred to a wastewater tanker for later treatment.

All equipment entering the borings and any tools used during the drilling process, including augers and samplers, were thoroughly decontaminated between borings using a heated pressure washer at a decontamination pad located near the northwest side of Building 25. All fluids resulting from decontamination of equipment were transferred to the wastewater tanker located on site. Contents of the tanker were periodically transferred by OHM personnel to the wastewater treatment plant operated by OHM on Base. Drill cuttings were segregated and contained in a roll-off bin for characterization by Baker for appropriate disposal.

4.3 Well Configuration and Construction

The well-field configuration and well construction details for the test zone well field and recovery wells are described in Section 4.3.1. Installation and construction details for three multilevel samplers, two aquitard monitor points, and a Castle Hayne Aquifer

monitor well are described in Section 4.3.2. Tabulated well construction details and geologic logs for all wells are included in Appendix B.

4.3.1 Test Zone Wells and Recovery Wells

The injection, extraction and hydraulic control wells installed for the demonstration were designed and built for their specific functions during the PITT. The following paragraphs provide a brief description of the configuration, construction and completion of these wells.

The test zone well array is shown in Figure 4.1. The injection and extraction wells are configured in a divergent-flow, line drive pattern to induce flow of the injected fluids bi-directionally, i.e., divergently, from the centrally located line of injection wells towards the two lines of extraction wells.

Schematics of general well construction details for the injection and extraction wells are shown in Figures 4.2 and 4.3, respectively. The injection, extraction and recovery wells installed have an inside diameter of four inches and were constructed with a combination of Schedule 40 PVC casing and five-foot long stainless steel wire-wrapped screen with 0.01-inch slots. Flush-threaded stainless steel sumps, approximately five inches long, were installed at the bottoms of the wells. The injection wells were installed with two, five-foot screened intervals per well, one at the bottom of the well and one spanning the water table. The recovery wells were also completed with two screens per well, except for wells RW01 and RW02, which were installed with a single screen per well during Phase 2 for aquifer testing. Extraction wells were installed with only one screened interval located at the bottom of each well. The hydraulic control wells installed have an inside diameter of two inches and were constructed with a similar combination of Schedule 40 PVC and stainless steel screen. The hydraulic control wells were also constructed with two screened intervals per well, one at the bottom of the well and one spanning the water table. A summary of well completion details is provided in Table 3.1 (in Section 3.0).

Sand filter packs were installed around all well screens using Drilling Service Inc (DSI) #1 sand, which is approximately equivalent to 20/40 sieved sand. The filter packs were installed to a minimum of one to two feet above the well screens, as determined by measuring to the top of the filter packs with a weighted tape measure. One to two feet of 1/4-inch bentonite pellets were placed on top of the sand pack and hydrated with potable water. The bentonite seal was allowed to hydrate for a minimum of two hours before well construction continued. Dual screen wells required two sand filter packs and two bentonite seals per well to provide hydraulic separation between the upper- and lower-screen intervals. Concrete grout was then pumped into the remainder of the well annulus above the uppermost bentonite seal. The cement grout mixture consisted of four 50-lb bags of Bonsal Type I cement and 1/4 bag of high yield bentonite with water mixed into a 55-gallon drum.

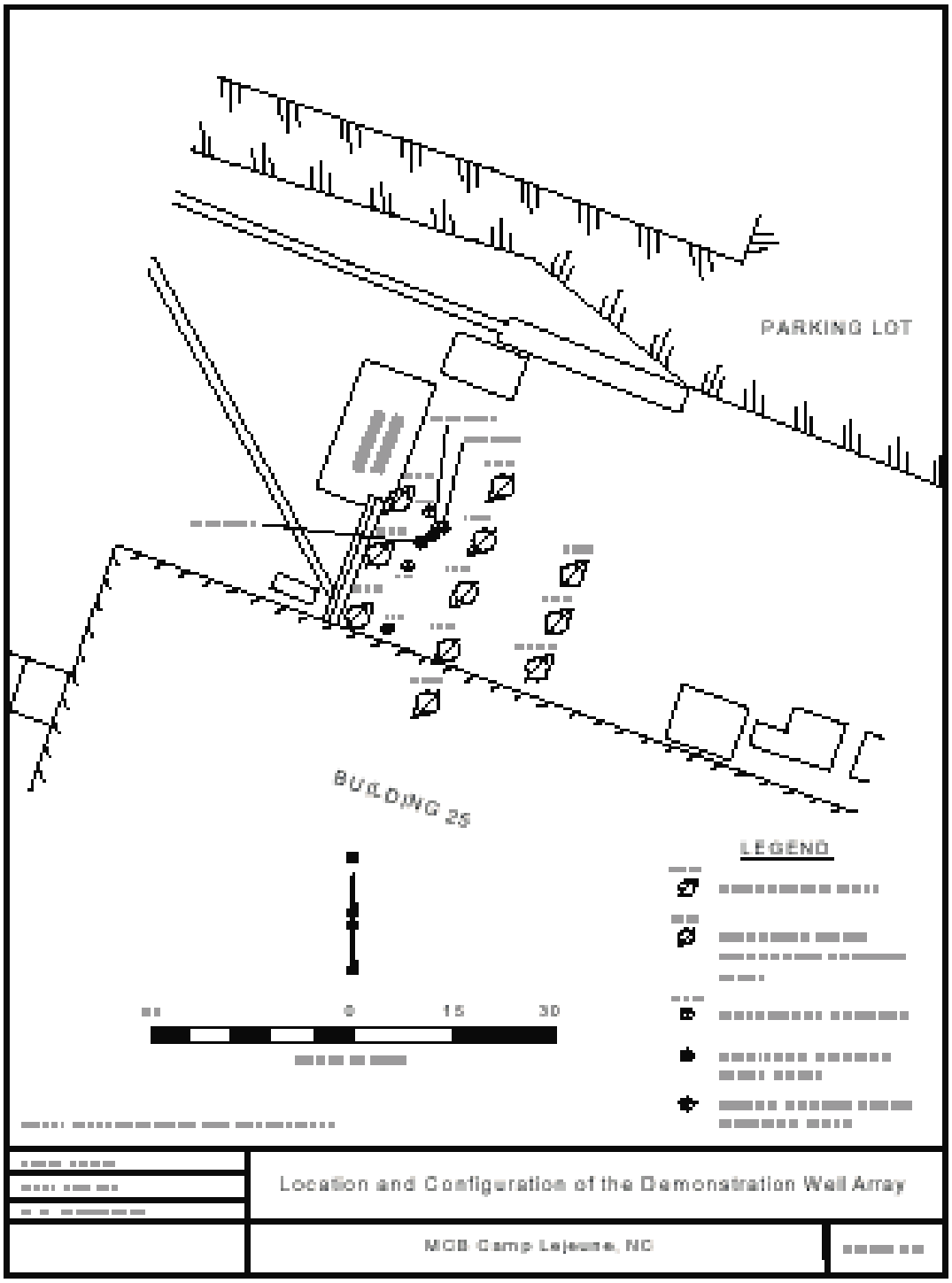

Figure 4.1. Location and Configuration of the Demonstration Well Array

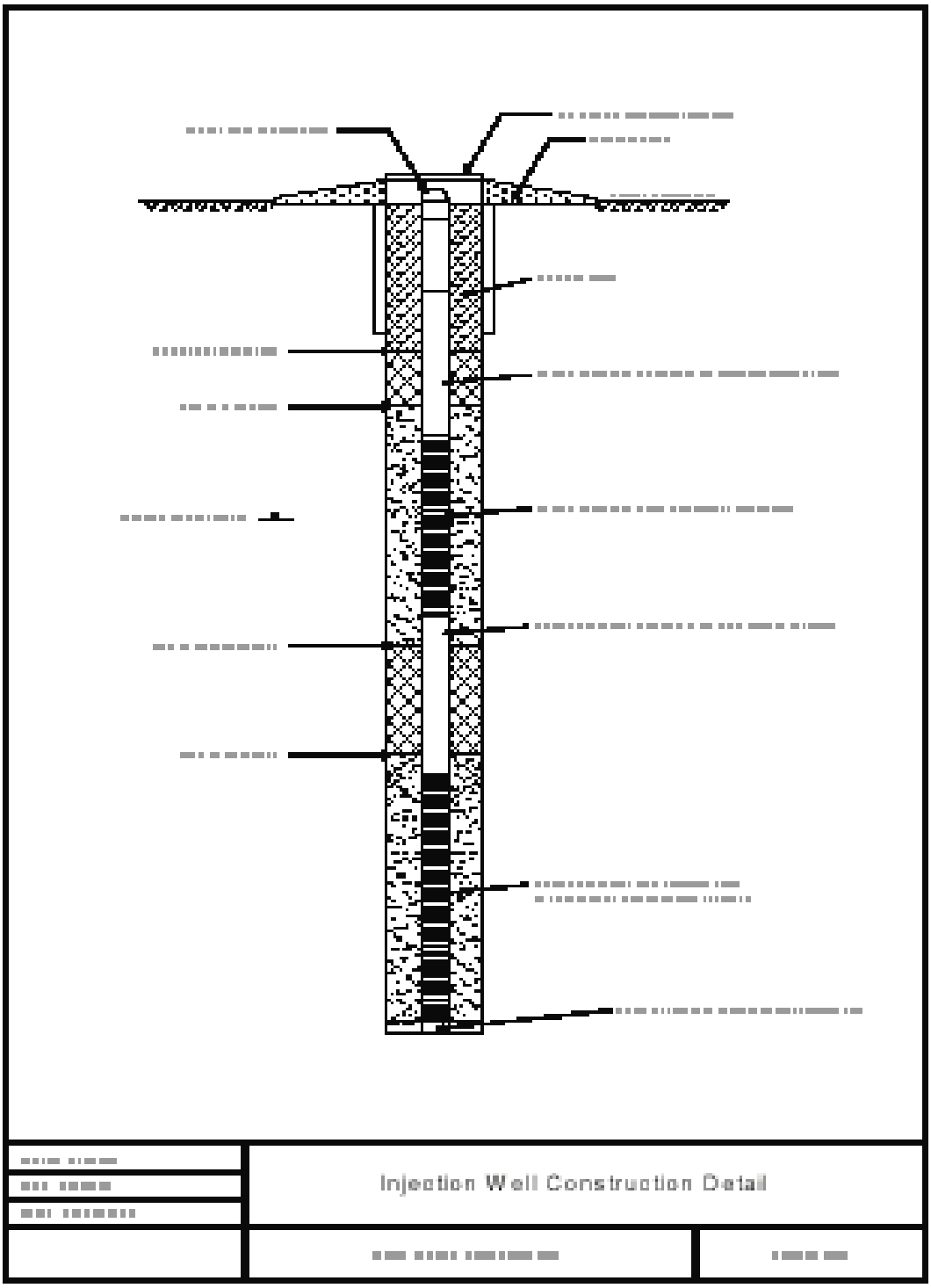

Figure 4.2. Injection Well Construction Detail

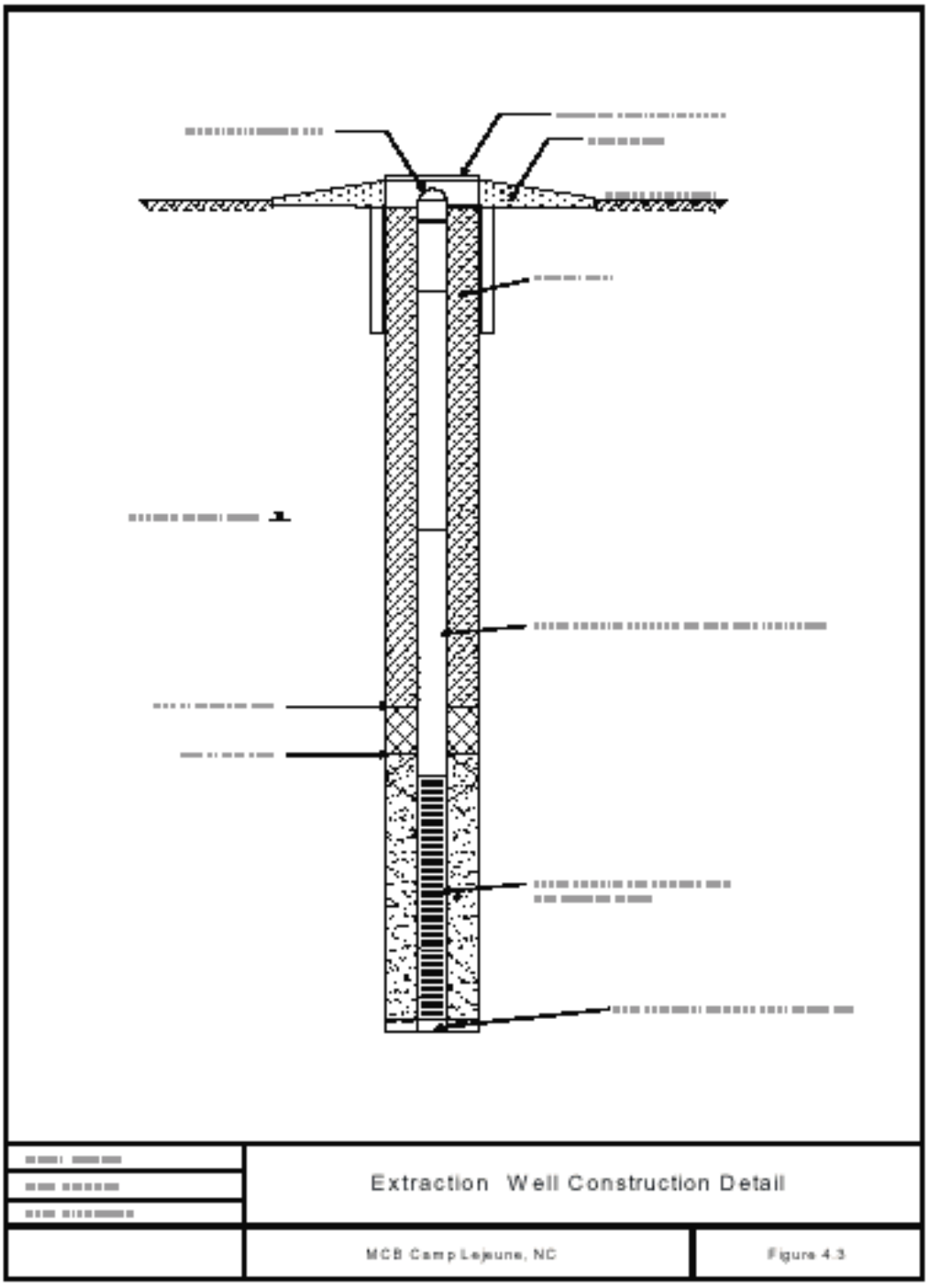

Figure 4.3. Extraction Well Construction Detail

Surface completions for all outside wells were constructed with two-foot square concrete pads and eight-inch flush mount covers. Surface completions for the wells inside Building 25 were constructed with six-inch flush mounted covers.

4.3.2 Multilevel Sampler Installations

Three multilevel samplers (MLS) were installed to monitor the interwell zone between the injection and extraction wells. Each MLS is located in-line between an injection and extraction well, approximately ten feet from the injection well and five feet from the extraction well. The MLS locations are shown in Figure 4.1, where MLS-1, MLS-2, and MLS-3 are located approximately five east of extraction wells EX01, EX02, and EX03, respectively.

Each MLS has three discrete sampling points to monitor the PITT and SEAR tests relative to depth; the sampling points are installed to monitor the bottom three feet of the DNAPL zone at approximately 17, 18.5, and 20 ft bgs. Each MLS sampling point is constructed with a porous cup (similar to an air stone) at the bottom, with 1/8-inch diameter stainless steel tubing connecting the porous cup to the surface for sampling. An MLS is composed of a bundle of three sampling points, with 1.5 feet between sampling points, as described above.

Each MLS bundle was installed by using a drill rig to push a 1.75-inch ID drill rod, with a sacrificial point on the end, into the aquifer to the desired total depth. The drill rod then functioned as a small diameter “drill casing” to hold the borehole open while the MLS bundle was lowered through the casing to the bottom of the hole. Then the drill rod (casing) was pulled out of the hole, leaving the sacrificial point at the bottom and allowing the aquifer to close in around the MLS sampling points. The upper portion of the borehole (which did not close), from approximately 8 ft bgs to the surface, was sealed with bentonite chips.

The bottom sampling point of each MLS bundle was installed approximately six inches above the clay aquitard, in the basal silt layer. The other two sampling points were installed above this, in the overlying fine sand and also in the transition zone between the basal silt and the overlying fine sand. The depth configuration of the MLS sampling points is shown in Figure 4.4, in the generalized cross section of the Site 88 geosystem.

4.3.3 Castle Hayne and Aquitard Monitor Points

After the PITT was completed, three additional monitor points were installed to prepare the SEAR demonstration area for the surfactant flood. Two well points were installed into the clay layer, and one well was installed into the Upper Portion of the Castle Hayne Aquifer to monitor for possible downward migration of surfactant fluids into the aquitard or into the Upper Portion of the Castle Hayne Aquifer during the upcoming surfactant flood.

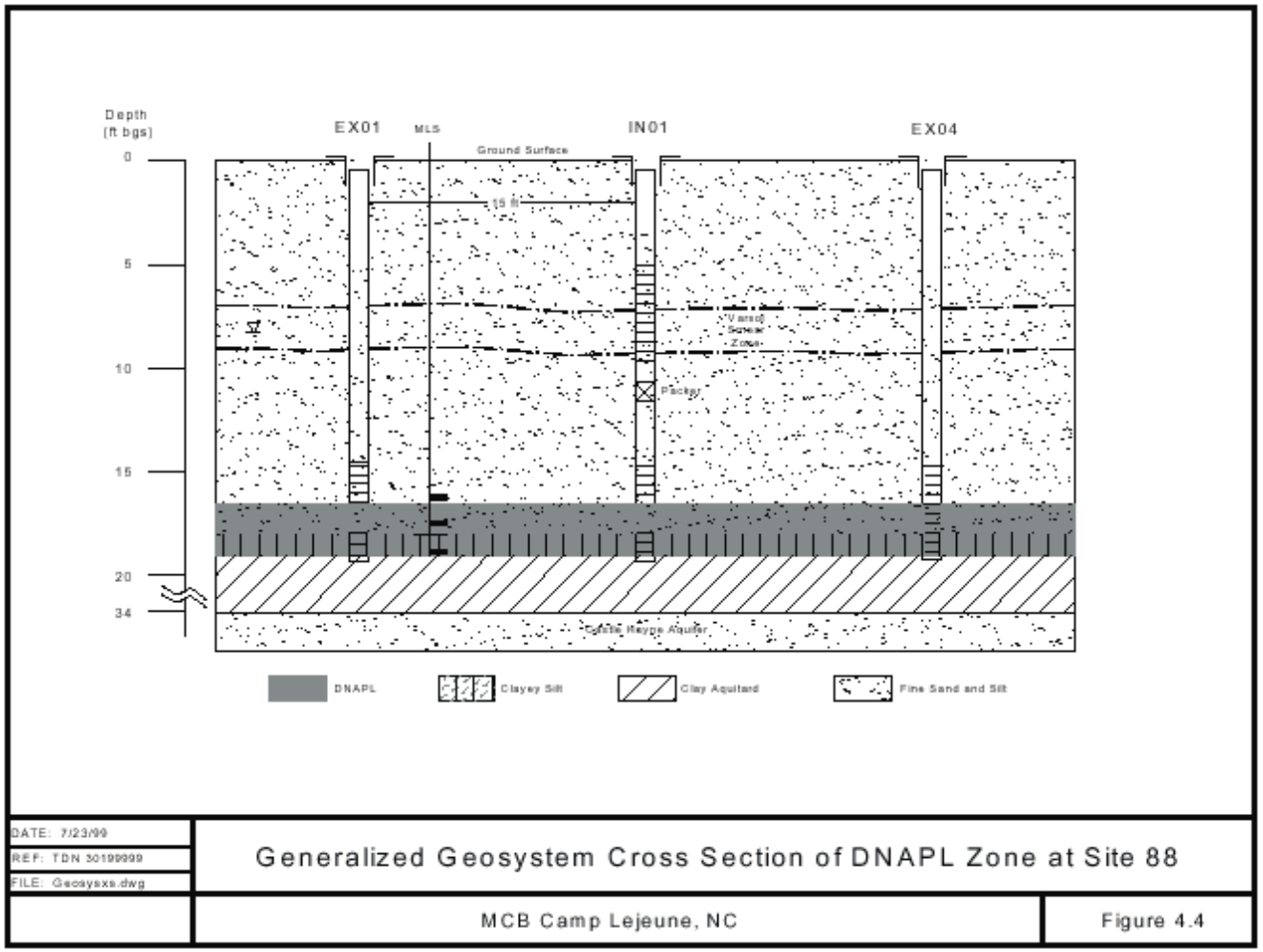

Figure 4.4. Generalized Geosystem Cross Section of DNAPL Zone at Site 88

The aquitard well points, WP01AQT and WP02AQT, were constructed with Geoprobe implant screens that are pushed into the ground with a Geoprobe drive casing and a sacrificial drive point at the bottom. Each well point consists of a small screen, approximately 0.5-inch diameter X 12-inches long, which is connected to the surface with 0.25-inch diameter Teflon®-lined plastic tubing. The well points were installed through a three-inch diameter steel pipe which was pushed into the approximately 1.5-2 feet clay aquitard as a surface casing for the well-point installations.

The Castle Hayne monitor well, MW10IW, was also completed through a surface casing. The surface casing was installed through the shallow aquifer and sealed at the upper surface of the clay aquitard with bentonite and grout to protect from potential downward migration of contaminants via the well installation. The well was completed with a five-foot screen length into the Upper Portion of the Castle Hayne Aquifer, just below the lower contact of the clay aquitard.

4.4 Well Development

After all the wells had been installed, a minimum of 24 hours was allowed to pass before each well was developed. To develop each well, a surge block was used to force water across consecutive 1.5-foot sections of the well screen and filter pack. A Watera pump was used to periodically evacuate the wellbore of sediment-laden ground water. The progress of the development effort was monitored by observing the amount of sediment in the purge water and measuring the pH, conductivity, and temperature of water samples collected from the Watera pump after each borehole volume of water was removed from the well.

A well was considered to be developed when at least three borehole volumes had been removed from the well, the purge water was relatively free of sediment, and the pH, conductivity, and temperature had stabilized to within 10% of the previous set of readings. The water produced at each well during development was collected in 55-gallon drums, and then transferred into the onsite wastewater tanker.

5.0 SITE GEOSYSTEM

After all the data from the DNAPL investigations was evaluated, it was compiled and interpreted to construct the site geosystem. The site geosystem is the basis of the model used for PITT design simulations with UTCHEM.

The geosystem is primarily composed of, but not limited to, the following site-specific properties:

- physical and chemical properties of the aquifer (hydrostratigraphy, permeability, and mineralogy);
- ground-water chemistry of the aquifer (organic and inorganic solutes);
- physical properties of the capillary barrier (aquitard); and
- physical and chemical properties of the DNAPL: density, viscosity, interfacial tension, chemical composition, and spatial distribution of the DNAPL.

The geosystem of the test zone at Site 88 is described below.

The test zone is in a shallow unconfined aquifer. This aquifer is bound at its base in the demonstration area by a clay layer of variable thickness that separates it from the underlying Castle Hayne Aquifer. The sediments of the shallow aquifer consist of fine to very-fine sands, grading with depth into a clayey-sandy silt directly overlying the clay layer. The top of the clay layer is found at a depth of approximately 19 to 20 ft bgs. Since the depth to water in the shallow aquifer is approximately 8 ft, the saturated thickness of the aquifer is on the order of 11 to 12 ft. The results of a short-term constant rate pumping test, discussed in Section 3.2, show the average hydraulic conductivity of the aquifer to be $5x10^{-4}$ cm/sec (1.4 ft/day). Results from MLS samples collected during the PITT show that the hydraulic conductivity of the basal clayey-sandy silt is lower than that of the overlying fine sands by a factor of approximately four. This implies a hydraulic conductivity of $1x10^{-4}$ cm/sec (0.4 ft/day) for the basal silt layer.

Two soil samples were collected at soil boring IS-25 for analysis by x-ray diffraction to determine mineral percentages of the shallow aquifer. The samples, collected at depths of 17.2 and 19.1 ft bgs, show very similar mineralogy. Both samples were greater than 80% quartz with some feldspar and pyrite. Clay minerals comprised 7% and 9% of the samples respectively with kaolinite, illite, chlorite, and smectite all represented. The XRD analyses were performed by PTS Laboratories, Houston, Texas; the laboratory report is included in Appendix E.

The characterization of organic and inorganic solutes in the site geosystem are discussed in Section 3.3, but are summarized as follows. The organic solutes are

predominately PCE, which is reported as high as 170 mg/L in the test zone (Table 3.5). With respect to inorganic solutes, the ground water is characterized as having low total dissolved solids, ranging from about 160 to 170 mg/L, based on the major ions reported in Table 3.6.

Ground-water flow in the shallow aquifer in the vicinity of the PITT/SEAR demonstration area is generally to the southwest, as shown in Figure 5.1. The figure shows that the ground-water gradient is relatively low in the immediate area of the demonstration but increases to the southwest.

The underlying Castle Hayne Aquifer is confined in the immediate area of the investigation. Ground-water levels in the Upper Portion of the Castle Hayne are on the order of seven feet lower than those in the shallow aquifer, producing a vertical hydraulic gradient across the clay layer separating them. Wells completed in the vicinity of the demonstration area show that the sediments of the Upper Portion of the Castle Hayne Aquifer are fine to medium sands. The Castle Hayne Aquifer is used as a regional source of potable water.

One of the primary concerns in a DNAPL-contaminated field site is the vertical migration of the DNAPL. Such vertical migration is usually arrested by the presence of clay aquitards, which have much lower permeabilities than the aquifer materials. The lower permeabilities impart a greater ability to resist further invasion and migration of DNAPL. This also accounts for the pooling of DNAPL at greater than residual saturations above formations with low permeabilities, i.e., a capillary trap. The ability of an aquitard to prevent entry and downward flow of DNAPL is determined by the pore size distribution of the medium, the head of DNAPL on the aquitard, and the wetting nature of the mineral surfaces in contact with the DNAPL.

The clay layer separating the shallow aquifer from the Castle Hayne Aquifer is variable in thickness. Figure 5.2 shows the elevation of the top of the clay layer, as determined from soil cores and cone penetrometer logs. The dominant feature to be noted on the figure is the depression in the clay surface. It is this depression in which the PCE DNAPL has accumulated.

A number of cone penetrometer pushes were completed through the clay layer to determine the aquitard thickness. These pushes were located outside the area of known residual- and free-phase DNAPL contamination as determined by detailed soil sample collection and analysis. This information was combined with soil logging data to establish the depth to the bottom of the clay layer and hence its total thickness. Figure 5.3 shows the total thickness of the aquitard, which is greater than 12 ft thick in the demonstration area. However, it does decrease in thickness significantly to the southwest.

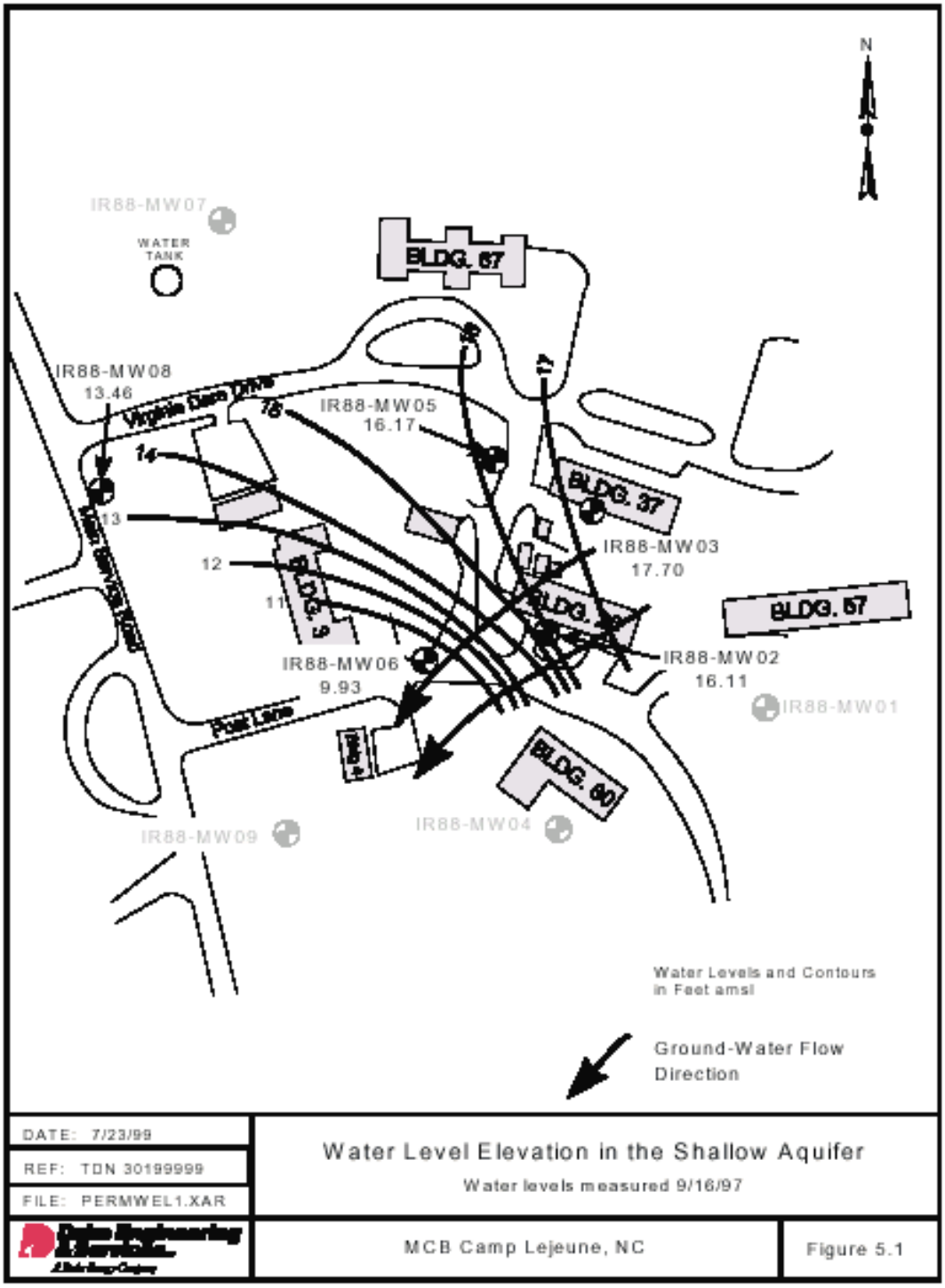

Figure 5.1. Water Level Elevation in the Shallow Aquifer

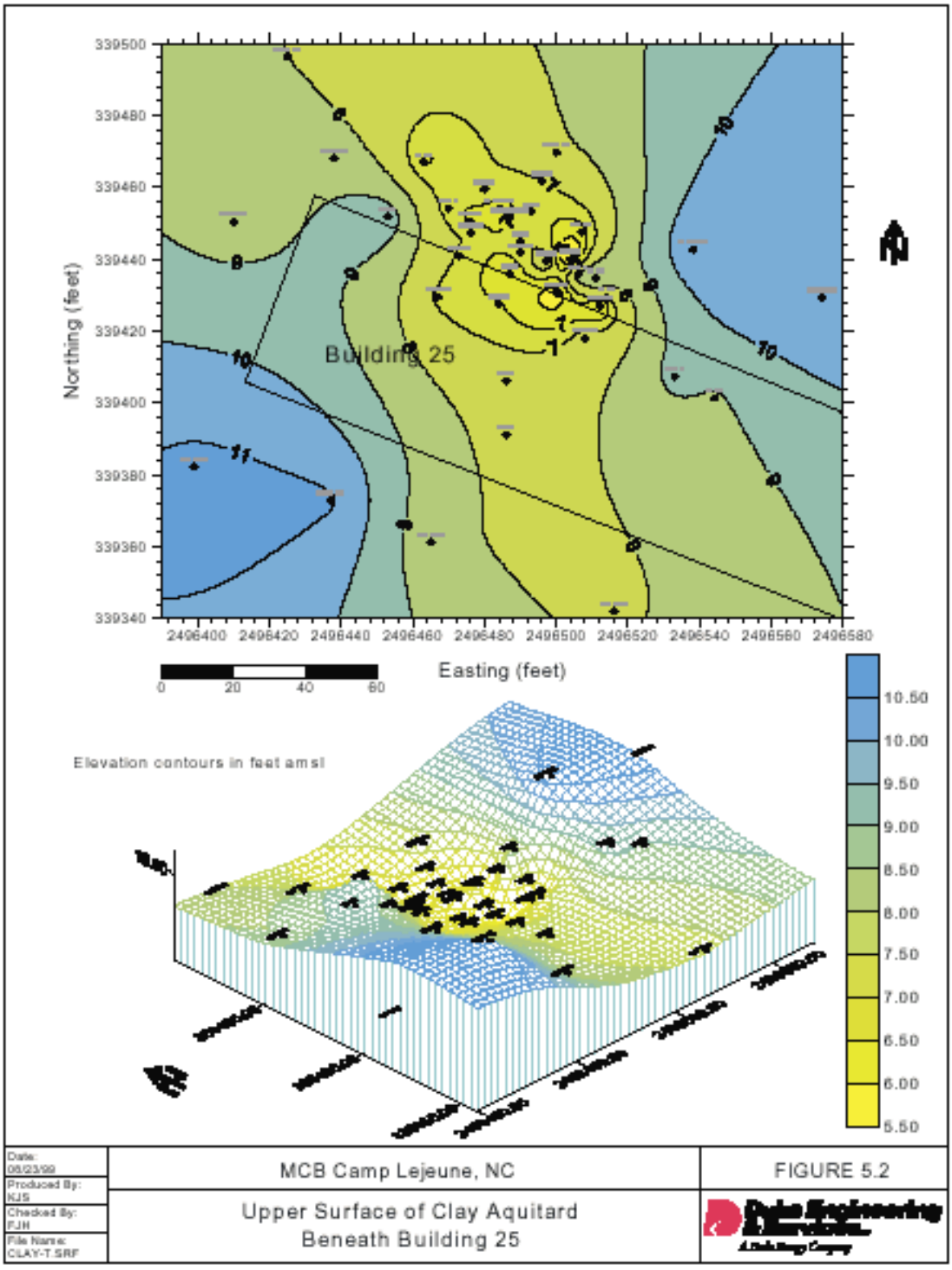

Figure 5.2. Upper Surface of Clay Aquitard Beneath Building 25

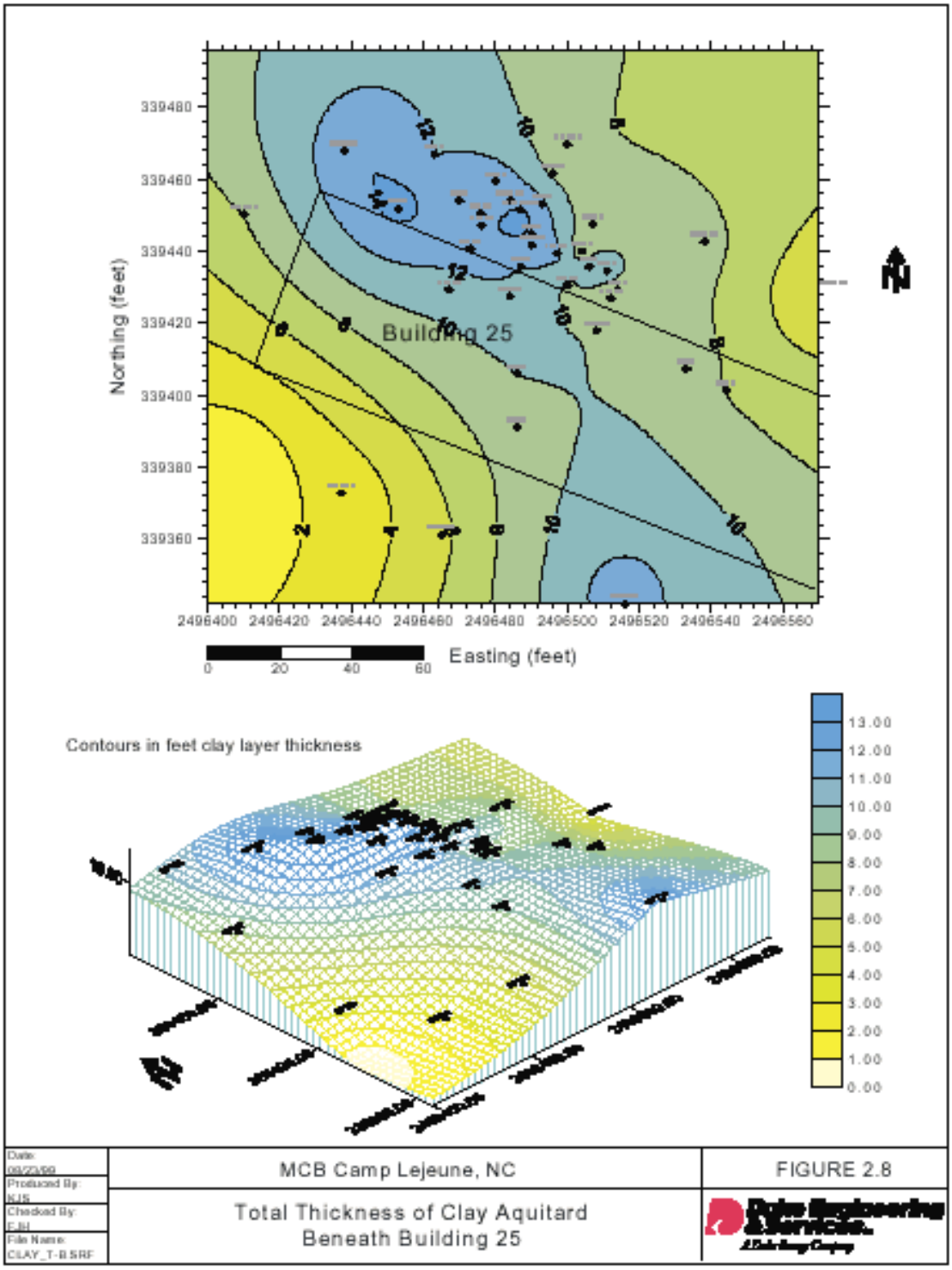

Figure 5.3. Total Thickness of Clay Aquitard Beneath Building 25

Samples of the clay layer were collected and submitted for vertical hydraulic conductivity, porosity, and capillary pressure testing. Samples from two boring locations were submitted to PTS Laboratories in Houston, Texas for vertical hydraulic testing; IS22-06 at 21 ft bgs and IS23-04 at 19.5 ft bgs. The averaged results show a vertical hydraulic conductivity for the clay layer of 2.0×10^{-7} cm/sec (5.6×10^{-4} ft/day) which compares favorably with the 1.0×10^{-4} ft/day reported in the RI (Baker, 1998a).

Clay samples from the boring at well IN01 were submitted to TerraTek, Salt Lake City, Utah for porosity and capillary pressure tests. The measured porosity for the IN01 sample at 21.1 ft bgs was 49.6%. The results of the capillary pressure experiment for the IN01 sample at 21.0 ft bgs show that the aquitard is an effective capillary barrier that can support up to 20 ft (6 m) of PCE-DNAPL while allowing negligible DNAPL penetration.

For further details, see Appendix I, which includes a discussion of capillary effects at DNAPL sites, data analysis and interpretation of the capillary pressure test, and laboratory reports for the vertical hydraulic conductivity, porosity, and capillary pressure tests.

5.1 DNAPL Distribution

More than 100 soil samples were collected during the investigative phase and analyzed for the presence of VOCs. These samples were preserved in methanol in the field to minimize losses through volatilization. The results of the soil core VOC and NAPLANAL analysis, as presented in Section 3, reveal trends in the vertical and horizontal distribution of DNAPL. The majority of the DNAPL was at depths greater than 15 ft bgs. The results also indicate that once encountered, DNAPL saturations increase with depth until the clay layer (aquitard) is encountered. DNAPL saturations are generally greatest just above the aquifer/aquitard interface and along the top of the clay layer. Samples collected deeper in the clay exhibit a sharp decline to non-detect with depth. This supports the assumption that the clay layer is acting as a capillary barrier, effectively restricting the downward migration of PCE. The occurrence of DNAPL and Varsol™ in the test zone is shown in Figure 4.4, a generalized cross section of the geosystem.

The data is consistent with a scenario in which the DNAPL migrated laterally into the test zone along the sloping surface of an aquitard from a limited number of vertical migration pathways bringing the DNAPL down from the entry location to the aquitard. DNAPL that migrated into the test zone in this way would be encountered near the aquifer/aquitard interface with little or no DNAPL found higher in the shallow aquifer. The vertical migration pathways are likely beneath the building, outside the test zone.

6.0 FREE-PHASE DNAPL RECOVERY AT SITE 88

Free-phase DNAPL has been observed in a number of the wells installed at Site 88 during the DNAPL source-zone investigations. Recall from Section 1.2 that *free-phase* DNAPL is defined as DNAPL existing in the subsurface under a positive pressure such that it can flow into a well. In contrast, *residual* DNAPL occurs at a lower DNAPL saturation as disconnected ganglia that are held in the pore spaces by capillary forces. Residual DNAPL is not free to flow into a well. Free-phase DNAPL accumulation should be removed, to the extent possible, from the test zone before conducting a PITT in order to improve the accuracy of the PITT. PITTs are designed to measure the volume and saturation of residual DNAPL in the test zone and the presence of free-phase DNAPL reduces their accuracy (see Jin et al., 1997).

Table 6.1 lists the wells that have produced free-phase DNAPL and the approximate depth to the DNAPL/water interface in each well before DNAPL recovery operations were initiated. Plots of the DNAPL/water interface elevations during all field activities can be found in Appendix J.

Table 6.1 DNAPL Levels in Wells at Site 88

Well	Depth to DNAPL (ft BTOC)	DNAPL Elevation (ft amsl)	Approx. DNAPL Thickness (ft above top of clay)
EX01	17.1	8.5	1.6
EX02	20.2	5.4	> 0.3 *
IN01	19.4	6.3	0.3
HC01	21.0	5.4	> 0.3 *
RW01	18.6	6.6	> 0.3 *
RW02	18.2	7.2	0.5
RW04	17.2	8.6	2.8
RW06	16.8	9.7	2.3

***** DNAPL was consistently present in these wells, but the measured elevation of the water/DNAPL interface was equal to or less than the estimated elevation of the clay aquitard. It is not believed that the water/DNAPL interface is actually below the clay aquitard. The discrepancy is expected to lie in the soil coring and logging process. When soil cores are retrieved from a borehole for geologic logging (e.g. to determine the depth to clay), the recorded core depth for a given sample has a typical error of approximately ±0.3 ft bgs, and in some cases the error may be greater when sample recovery is less than 100%. Some error may also be associated with geologic interpretation.

In February 1998, a DNAPL recovery system was installed to remove as much free-phase DNAPL as possible from the test zone by pumping. Wells EX01, IN01, HC01, RW01, RW04, and RW06 were used as DNAPL recovery wells. The DNAPL recovery process was conducted in two stages. The first stage involved preliminary pumping of

DNAPL that had accumulated in the recovery wells with a peristaltic pump. This process began on February 18 and concluded on February 20.

A second stage of the DNAPL recovery process started immediately after completing the first stage and terminated in late March. It was conducted by pumping the six DNAPL recovery wells listed above simultaneously in order to create a hydraulic gradient, which would help to induce the free-phase DNAPL to flow to the recovery wells. The pumped fluids were composed primarily of contaminated ground water along with a much smaller component of DNAPL. The recovered wastewater/DNAPL was then transferred to the waste tanker on site. The pumping rate was controlled by keeping drawdown in the wells to a maximum of about four feet. The combined total flow from the six recovery wells to the tanker during recovery operations was approximately 1.3 gpm.

Attempts to quantify the volume of recovered DNAPL were generally unsuccessful. An interface probe was unsuccessful in measuring the depth of accumulated DNAPL in the bottom of the wastewater tanker; this was probably because the DNAPL levels in the bottom of the 8,800 gallon tanker were too shallow to be measured. Grab samples of effluent from the recovery wells were also collected in an attempt to volumetrically quantify the DNAPL recovery rate. Several five-gallon grab samples indicated that the effluent contained on average about 0.2% DNAPL and 99.8% ground water. However, modeling of DNAPL recovery under the site hydraulic conditions showed that DNAPL recovery could be expected to decrease over time; therefore, this method of measurement was not considered worthwhile due to the low, decreasing rates of DNAPL recovery.

Free-phase DNAPL recovery activities continued under water-flooding conditions (i.e., simultaneous injection and extraction operations) for 14 days during the CITT (April 15-28, 1998) and for 40 days during the PITT (May 13-June 22, 1998). During these periods, source water with 1000 mg/L $CaCl_2$ was injected continuously into IN01, IN02, IN03, HC01, and HC02, along with KBr as a tracer during the beginning of the CITT and alcohol tracers during the beginning of the PITT. Pumping was from the six extraction wells (EX01 to EX06), and there was no pumping from RW04 and RW06. CITT and PITT operations are discussed in detail in Sections 9 and 10.

It is believed that the total amount of DNAPL recovered at Site 88 is probably in the range of tens of gallons; about 30 to 60 gallons of DNAPL recovery is likely, and probably less than 100 gallons. The low permeability of the shallow aquifer greatly limits the rate at which free-phase DNAPL can be recovered by pumping. However, both free-phase and residual-phase DNAPL can be recovered by SEAR, i.e., their solubilization within a microemulsion formed by a surfactant-alcohol micelle and the solubilized DNAPL (Pope and Wade, 1995). This is the objective of the surfactant flood to be undertaken by the ESTCP team at Site 88 in 1999.

7.0 LABORATORY STUDIES AND TRACER SELECTION

7.1 Laboratory Scale Studies

This section of the report discusses the results from laboratory studies to measure the preliminary properties of the Camp Lejeune DNAPL and to select partitioning tracers for the PITT. All laboratory DNAPL studies discussed below were conducted with a DNAPL sample collected from well RW02, on August 22, 1997.

7.1.1 Preliminary Laboratory Studies

The preliminary studies focused on determining the physical properties of the DNAPL. These were necessary not only for the identification of DNAPL constituents, but also for the selection of tracers and surfactants. The density of the DNAPL was measured using a pycnometer; the procedure is included in Appendix K. This measurement was done three times to ensure repeatability. The density of the field DNAPL sample from Site 88 was 1.588 g/cm^3. This is very close to the density of pure PCE (1.63 g/cm^3) which suggests that the DNAPL contained a small fraction of dissolved mineral oils and grease.

The viscosity of the DNAPL was measured using a Contraves low shear viscometer. The measurement of the viscosity of deionized water was used as a means for ensuring quality control. The measured viscosities of the Camp Lejeune DNAPL sample varied between 0.85 centipoise and 1.10 centipoise between shear rates of 0.01 sec^{-1} and 128 sec^{-1}. The viscosity of deionized water under similar conditions was measured at 0.9 centipoise, which agrees with the value reported in the literature.

A spinning drop tensiometer (Cayais et al., 1975) was used to measure the interfacial tension (IFT) between the Site 88 DNAPL and water. This instrument has been used extensively by the petroleum industry to measure IFTs down to 10^{-3} dyne/cm. The IFT between the Site 88 DNAPL and water was measured at 10.36 dynes/cm. This is much lower that the IFT between PCE and water of 47.48 dynes/cm (Demond and Lindner 1993). This suggests that the DNAPL may have dissolved surface/active agents which bring about a lowering in the IFT, or that the low IFT is caused by the solubilized oil and grease noted above.

7.2 Partitioning Tracer Selection

When selecting PITT tracers for field applications, there are a number of tracer performance criteria that must be met. These include:

- Environmental acceptability

- Chemical and biological stability
- Insensitivity to small variations in the composition of the DNAPL
- Low detection limits
- Cost effectiveness
- Reasonable market availability

Aliphatic alcohols fulfill all the above performance criteria and are commonly used by DE&S as partitioning tracers. Theoretically, only two tracers, one nonpartitioning and one partitioning, are required for an interwell test. In practice, however, a suite of tracers with different partition coefficients is used to improve the accuracy of the tracer test results. This is especially true when there is a large range of uncertainty in the quantity and distribution of the DNAPL in the pore space to be swept by the test, because the partition coefficient of each alcohol effectively controls how fast that tracer moves across the test zone in the presence of DNAPL. If the residual saturation is known to be relatively high, tracers with smaller partition coefficients are sufficient, and it is not mandatory to continue the test to obtain the response curves for the tracers with larger partition coefficients. If the residual saturation is lower than expected, the tracers with larger partition coefficients can ensure good separation of the tracer response curves, thereby giving a better estimate of DNAPL saturation. Aliphatic alcohols fulfill these criteria and have been used in several PITTs (Jin, 1997a, b; Young et al., 1999; Annable et al., 1998).

This section of the report presents the results of partition coefficient measurements conducted to identify the partitioning tracers required for the PITT at Site 88. The objective of these experiments was to determine the partition coefficients of the alcohol partitioning tracers between the Site 88 DNAPL and water. This section also contains the results of a series of soil column partitioning tracer experiments designed to evaluate the performance of each of these candidate partitioning tracers in both contaminated and uncontaminated aquifer sediment from Site 88.

7.2.1 Measurement of Static Partition Coefficients

The individual tracers in the PITT tracer suite are chosen on the basis of their partition coefficients given the travel time through the swept pore space during a PITT. The partition coefficients of the tracers chosen for a PITT should result in a retardation factor of between 1.2 and 4.0 to obtain good separation of the nonpartitioning and partitioning tracers for a reasonable test duration (Jin et al., 1995). Previous site investigations in the source area indicate that DNAPL is mainly present on top of the capillary barrier at the base of the shallow aquifer. Therefore, tracers with larger partition coefficients were needed for DNAPL estimation since much of the injected

tracer will flow through the uncontaminated sediment above the DNAPL and be relatively unaffected by the presence of the DNAPL. Static or batch partition coefficient experiments were conducted with the DNAPL sample from Site 88 and a total of six aliphatic alcohols were selected. Some experiments were also conducted with stock PCE to ensure quality control of the experimental measurements. This was done to ensure that tracers with an acceptably wide range of partition coefficients were identified for use in the PITT.

The accurate measurement of tracer partition coefficients is critical for the success of a PITT. The partition coefficient (K_i) for a tracer 'i' is defined as:

$$K_i = \frac{C_{i,DNAPL}}{C_{i,water}} \qquad (7.2.1\text{-}1)$$

where:

$C_{i,DNAPL}$ = equilibrium concentration of the tracer 'i' in the DNAPL (mg/L)
$C_{i,water}$ = equilibrium concentration of the tracer 'i' in the aqueous phase (mg/L)

The accuracy of the experimental measurements was checked by using the equivalent alkaline carbon number (EACN) approach, developed by Dwarakanath and Pope (1998) to estimate partition coefficients. Both the measured and estimated static partition coefficients are presented in Table 7.1. A close match between the measured and predicted static partition coefficients is observed, within the experimental uncertainty, suggesting that the accuracy of the partition coefficient measurements was acceptable.

Table 7.1 Partition Coefficients of Alcohols with Camp Lejeune Site 88 DNAPL

Alcohol	Measured Partition Coefficient	% Uncertainty	Estimated Partition Coefficient
1-Methanol	0.0	--	0.1
1-Propanol	0.0	--	0.1
4-Methyl-2-Pentanol	4.2	3.8	4.4
1-Hexanol	8.1	3.6	7.6
2-Ethyl-1-Butanol	6.0	3.9	5.7
5-Methyl-2-Hexanol	24.1	8.7	24.4
1-Heptanol	35.0	9.3	34.5
2-Ethyl-1-Hexanol	115	2.6	115

7.2.3 Soil Column Experiments

Once the partition coefficients of several candidate partitioning tracers were identified using the static partition coefficient experiments, their behavior in the presence of Site 88 soil and DNAPL was evaluated under dynamic conditions in soil column experiments. The approach used was to first conduct partitioning tracer experiments in columns containing uncontaminated shallow aquifer material from the test site at Camp Lejeune. In these experiments 1-propanol was used as the conservative tracer. The relative retardation of the partitioning tracers with respect to 1-propanol was measured and the apparent DNAPL saturation caused by tracer sorption was estimated. Partitioning tracer experiments were then conducted in columns with a known volume of DNAPL to determine their ability to accurately estimate the volume of DNAPL under dynamic conditions in the presence of Site 88 aquifer sediments. Two column experiments in uncontaminated Site 88 sediments and two column experiments in DNAPL-contaminated sediments were conducted to evaluate the performance of the partitioning tracers. The experimental procedures followed for the soil column experiments are presented in Appendix K, as well as the techniques used to analyze the data from the experiments. The results obtained from the soil column experiments are presented below.

7.3 Results from Soil Column Experiments

This section discusses the results from laboratory partitioning tracer experiments in both contaminated and uncontaminated aquifer sediments from Site 88, and discusses the implications of these results in the analysis and interpretation of field partitioning tracer data.

7.3.1 Partitioning Tracers in Uncontaminated Soil

Partitioning tracer experiments were conducted in uncontaminated soil in columns CLJ#1 and CLJ#2. The main purpose in conducting these experiments was to determine whether naturally occurring organic matter would interfere with the accuracy of DNAPL measurement by partitioning tracers. During initial floods through the Site 88 soil columns, plugging by clay fines was observed. This problem was alleviated by the addition of 0.1% $CaCl_2$ to the injected solutions of tracer and water. Thus, in all subsequent soil column experiments, $CaCl_2$ was included as a constituent of the injected solution. The tracer response curves for both these experiments in uncontaminated soils are shown in Figure 7.1. Reference to this figure suggests that partitioning tracers such as 1-hexanol and 1-heptanol are retarded with respect to the conservative tracer 1-propanol. The heavier alcohol tracers with higher partition coefficients show a greater degree of retardation compared to the lighter alcohol tracers. The method of moments, as discussed in Appendix K, was used to estimate

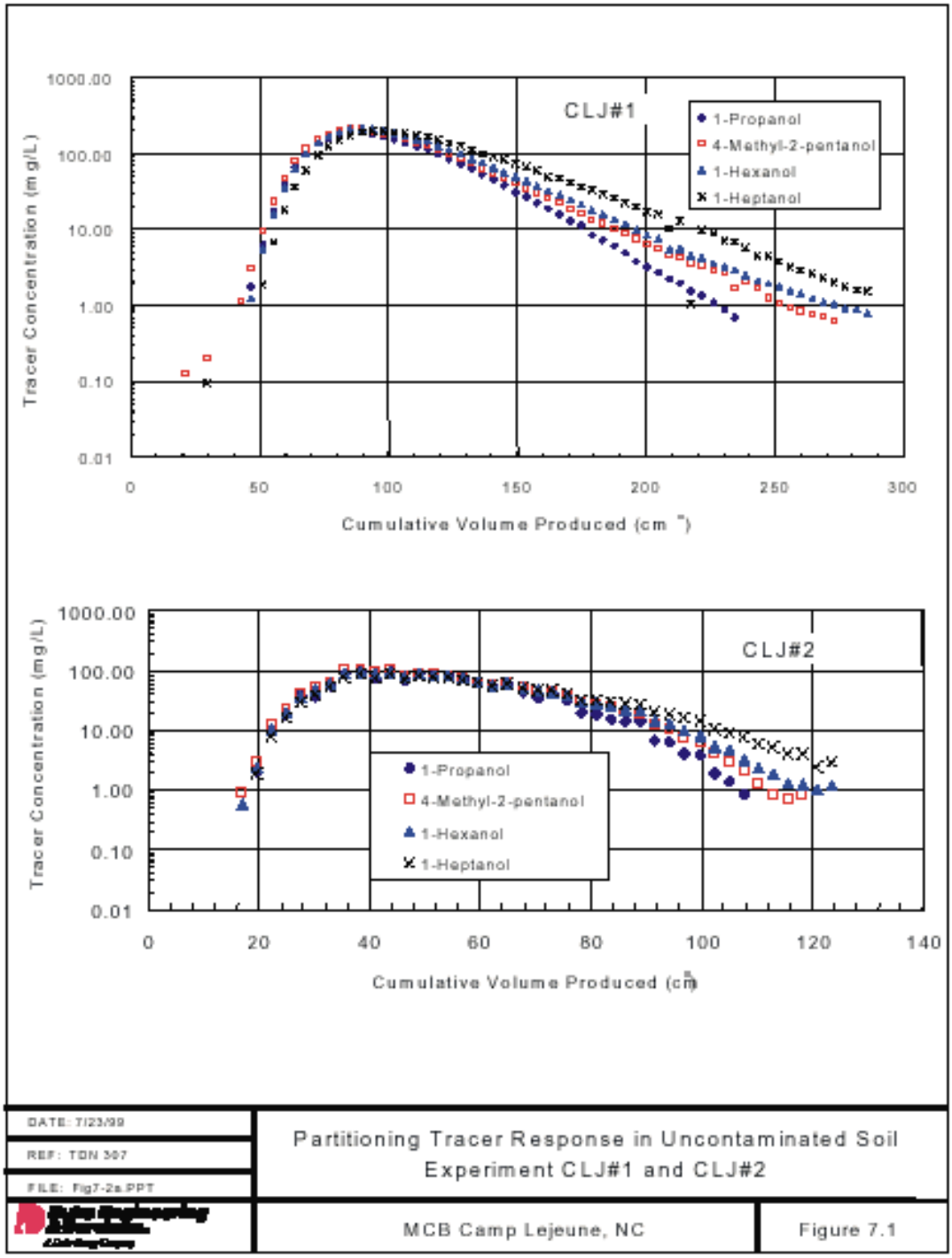

Figure 7.1. Partitioning Tracer Response in Uncontaminated Soil, Column Experiments CLJ#1 and CLJ#2

the apparent DNAPL saturation and the retardation of the partitioning tracers in the column tests.

Both the tracer retardation and the estimated DNAPL saturation, using the measured DNAPL partition coefficients, are given in Table 7.2. Based upon these experimental observations it is evident that both columns have an apparent DNAPL saturation between 0.3% and 0.5%. This apparent detection of DNAPL by the partitioning tracers can be attributed to the adsorption and retention of the partitioning tracers by the sedimentary organic carbon in the aquifer sediments. Such retention of partitioning tracers has been observed in uncontaminated aquifer material from other sites (Edgar, 1997). Interference by sorption to sedimentary organic carbon is typically significant in sediments with f_{oc} values greater than about 1000 mg/kg (Schwarzenbach and Westall, 1981). The f_{oc} of Site 88 soil samples used in these column experiments ranged from 1200 to 2100 mg/kg, with a visible component present as small peat particles. This will account for the observed retardation (Figure 7.1) due to sorption of the partitioning tracers to sedimentary organic carbon despite the absence of DNAPL. A detailed description of the retardation of the partitioning tracers by uncontaminated soils in laboratory column experiments and an experimental correlation between the f_{oc} and the retardation of the partitioning tracers is given in Edgar (1997).

Table 7.2 Retardation of Partitioning Tracers in Uncontaminated Camp Lejeune Soil

Column	Tracer	Retardation	Apparent DNAPL Saturation (%)
CLJ#1	4-Methyl-2-Pentanol	1.015	0.38
	1-Hexanol	1.025	0.31
	1-Heptanol	1.119	0.34
CLJ#2	4-Methyl-2-Pentanol	1.025	0.50
	1-Hexanol	1.035	0.44
	1-Heptanol	1.137	0.39

7.3.2 Partitioning Tracers in Contaminated Soil

Partitioning tracer experiments were conducted in columns CLJ#2 and CLJ#3 after both columns were contaminated with the Site 88 DNAPL. The main purpose of conducting these experiments was to determine the ability of the partitioning tracers to accurately estimate the residual DNAPL saturation. An additional objective of these experiments was to determine an adequate residence time for the partitioning tracers in the subsurface. Providing an adequate residence time for the tracers in the subsurface during a PITT is essential because this allows the partitioning tracer molecules to partition into and out of the trapped DNAPL and reach equilibrium. Nonequilibrium partitioning should be avoided since it can lead to incomplete characterization of the tail

portions of partitioning tracer breakthrough curves, which can potentially cause errors in estimating the DNAPL saturation.

Based upon mass balance measurements, the DNAPL saturation in column CLJ#2 was 5.06%, and 6.35% in column CLJ#3. The response of the partitioning tracers is shown in Figure 7.2. The tracer breakthrough curves show retardation of the partitioning tracers with respect to the conservative tracer 1-propanol. This is an indication of the presence of DNAPL. The method of moments, as discussed in Appendix K, was used to estimate the DNAPL saturation. The estimates of DNAPL saturation based upon the method of moments for columns CLJ#2 and CLJ#3 are given in Tables 7.3 and 7.4. In column CLJ#2, an average DNAPL saturation of $4.42 \pm 0.50\%$ was estimated by the partitioning tracers compared to the mass balance value of $5.06 \pm 0.50\%$. Similarly in column CLJ#3, the tracer estimate of DNAPL saturation was $7.21 \pm 0.80\%$ compared to the mass balance value of $6.35 \pm 0.50\%$. Within experimental uncertainty, it is evident that the partitioning tracers can accurately determine the residual DNAPL saturation in Site 88 sediments.

Table 7.3 DNAPL Saturation Estimated by Partitioning Tracers, Column CLJ#2

Tracer Combination	DNAPL Saturation (%)
1-Propanol, 1-Hexanol	4.64 ± 0.55
1-Propanol, 2,4-Dimethyl-3-Pentanol	4.24 ± 0.46
1-Propanol, 1-Heptanol	4.40 ± 0.48
Average DNAPL Saturation (Tracers)	4.42 ± 0.50
Standard Deviation of Partitioning Tracer Estimates	4.2%
DNAPL Saturation by Mass Balance	5.06 ± 0.50

Table 7.4 DNAPL Saturation Estimated by Partitioning Tracers, Column CLJ#3

Tracer Combination	DNAPL Saturation (%)
1-Propanol, 1-Hexanol	7.02 ± 0.85
1-Propanol, 2,4-Dimethyl-3-Pentanol	7.17 ± 0.79
1-Propanol, 1-Heptanol	7.45 ± 0.78
Average DNAPL Saturation (Tracers)	7.21 ± 0.80
Standard Deviation of Partitioning Tracer Estimates	3.0%
DNAPL Saturation by Mass Balance	6.35 ± 0.50

These results also indicate that the residence times for the tracers during both these experiments are sufficient. The residence times for each tracer in the partitioning tracer experiments in columns CLJ#2 and CLJ#3 are shown in Table 7.5. The residence

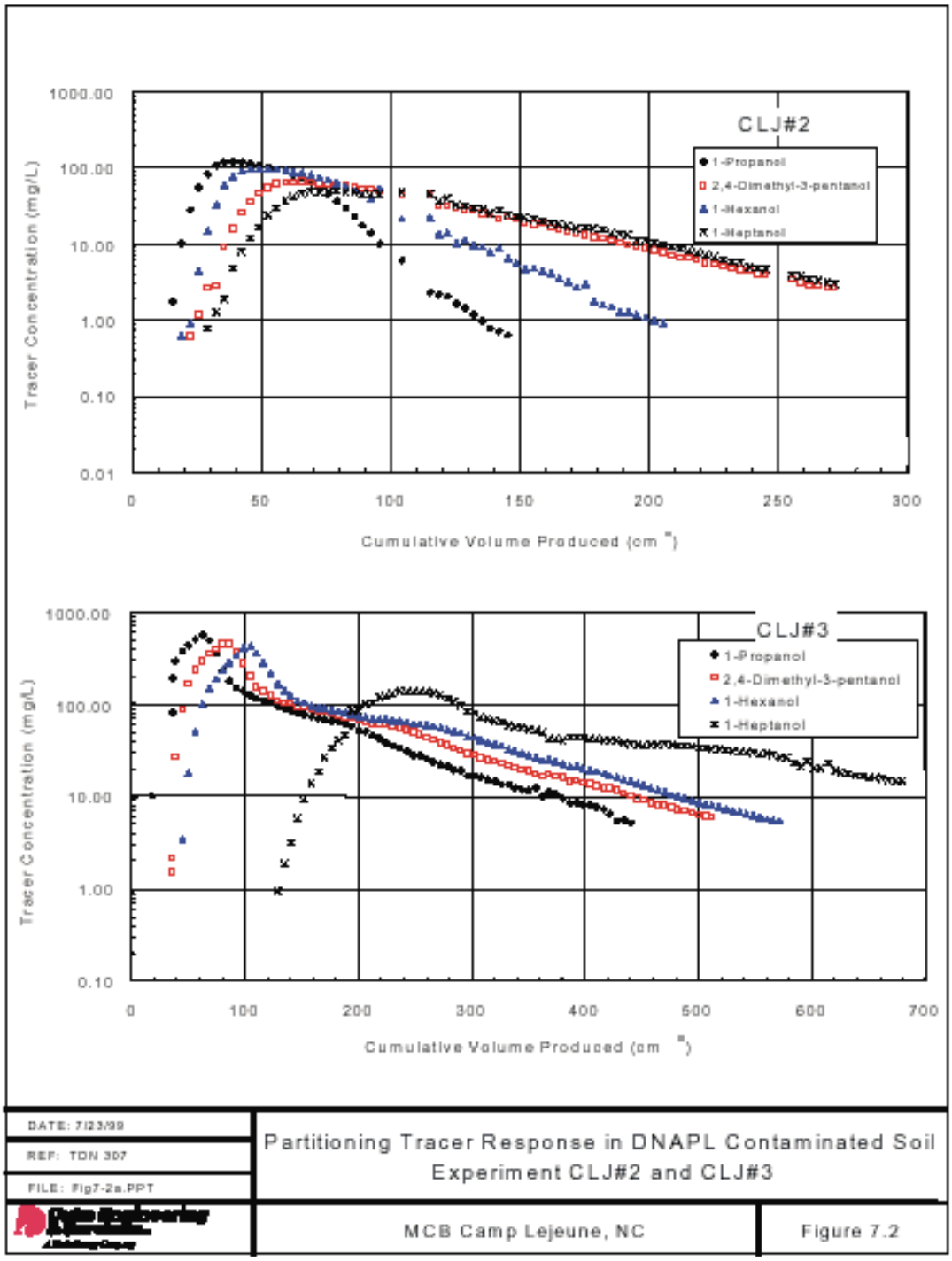

Figure 7.2. Partitioning Tracer Response in DNAPL Contaminated Soil, Column Experiments CLJ#2 and CLJ#3

times varied between 8 hours for the conservative 1-propanol to 26.7 hours for 1-heptanol. However a residence time of 9.5 hours was sufficient for 1-hexanol to accurately determine the DNAPL saturation in column CLJ#2. This suggests that a residence time of approximately 10 hours in the subsurface is adequate for equilibrium partitioning of the tracers.

Table 7.5 Residence Times for Tracers during Partitioning Tracer Experiments

Alcohol	Column	Residence Time (hours)
1-Propanol	CLJ#2	6.8
1-Hexanol	CLJ#2	9.5
2,4-Dimethyl-3-Pentanol	CLJ#2	15.3
1-Heptanol	CLJ#2	17.7
1-Propanol	CLJ#3	7.4
4-Methyl-2-Pentanol	CLJ#3	9.7
1-Hexanol	CLJ#3	11.8
1-Heptanol	CLJ#3	26.7

7.4 Tracers Selected for Further PITT Design

Based on the experimental results, and considerations such as cost and availability of the various compounds, the following tracers were selected for further PITT design: 1-propanol, 4-methyl-2-pentanol, 1-hexanol and 1-heptanol. More discussion of the tracer properties and quantities applied to the PITT design simulations is provided in Section 8.0.

7.5 Summary and Conclusions

From the results of the partitioning tracer column studies discussed above, it can be seen that retardation of the heavier alcohol tracers such as 1-heptanol in uncontaminated alluvium is greater than the average experimental error of 0.035 in the retardation factor (Dwarakanath, 1997). This is due to sorption of partitioning tracers to sedimentary organic carbon, which occurs primarily as peat particles in the Site 88 sediments. The presence of peat leads to a sedimentary organic content that is significantly greater than the f_{oc} typically found in aquifer sediments. The resulting sorption of partitioning tracers to the organic matter results in an apparent DNAPL saturation of between 0.3% and 0.5% in uncontaminated sediments. However, in contaminated sediments with relatively high DNAPL saturations, i.e., about 5% saturation, this effect was suppressed and no measurable errors were observed in the partitioning tracer estimate of the DNAPL saturation.

Based upon the soil column experiments conducted in this study, it can be inferred that the presence of DNAPL, at relatively high saturations, masks the effect of sorption by the organic material and hence can be neglected during the analysis of the partitioning tracer data. A number of wells in the test zone at Site 88, particularly those near the building, showed the presence free phase DNAPL. In these areas it can be assumed that the retardation of the partitioning tracers is dominated by the presence of high DNAPL saturations and is very weakly affected by the natural organic material. Hence the effect of retardation by the natural organic material in such areas can be neglected during the analysis of the field PITT data.

However, in other areas of the test zone, such as away from the building where DNAPL has not been observed, the natural organic matter may produce some degree of tracer sorption that will show an apparent presence of DNAPL at relatively low DNAPL saturations of about 0.4%. It is not known at this time what level of actual DNAPL contamination, i.e., average DNAPL saturation, is needed to dominate the tracer partitioning response in the presence of the sedimentary organic carbon at Site 88. Soil column testing at lower-level DNAPL saturations, i.e., <3%, is problematic with respect to obtaining an accurate weight (i.e. mass balance) for DNAPL added to a column, and is therefore prone to significant error at low DNAPL saturations.

The partitioning tracers evaluated in both DNAPL-contaminated column tests accurately predicted the residual DNAPL saturation. This can be concluded from the close agreement of residual DNAPL saturations based on mass balance and partitioning tracers. The standard deviation in the tracer estimates of residual DNAPL saturation was less than 5% in both the partitioning tracer column experiments indicating a high level of accuracy of the partitioning tracer method. The excellent agreement between mass balance and partitioning tracer estimates of residual DNAPL saturation also validate the accuracy of the static partition coefficient measurements. Finally, for this geosystem of alluvium and DNAPL, it can be concluded from the laboratory partitioning tracer experiments that a residence time of 10 hours is sufficient to allow for equilibrium partitioning of the tracers.

8.0 PITT DESIGN SIMULATIONS

Successful implementation of a PITT requires the development of an engineering design based on careful and systematic simulations. A good design should minimize the risk of failure, optimize the information collected, and save time and money. Simulation modeling before field test implementation can provide valuable insight into pertinent design parameters that affect the outcome of the tracer test. These design parameters include: the duration of the tracer test; the amount of tracer mass needed for injection; the number and configuration of injection, extraction, and hydraulic control wells; and injection and extraction flow rates for each well. To accomplish this, we used UTCHEM, which is a multi-component, multi-phase, three-dimensional chemical flood reservoir simulator developed at the University of Texas at Austin. It was originally developed to simulate the surfactant/polymer enhanced oil recovery process (Pope and Nelson, 1978; Datta-Gupta et al., 1986; Saad et al., 1990). In the past seven years, enhancements have been made to adapt UTCHEM to simulate both PITT and SEAR processes (Delshad et. al., 1996). UTCHEM represents the current state of the art for PITT and SEAR design, and has been successfully used by DE&S (formerly INTERA) in the past several years to design numerous PITT, surfactant, and surfactant/foam flood field demonstrations (e.g., INTERA, 1997b; Jin et al., 1997a, b; RICE et al, 1997).

8.1 PITT Design Strategy and Modeling Approach

The first step in designing a tracer test with a numerical simulator is to set up a three-dimensional model of the test zone using an appropriate geometry and grid. Input parameters to the model should include the best available estimates of the site geosystem components, such as the permeability field, porosity, multi-phase fluid densities and viscosities, dispersivity and other site-specific properties based upon data from site investigations or from similar geosystems by analogy. After the model has been developed, a number of sensitivity analysis simulations are conducted to simulate the performance of the test to provide an optimum design for the PITT. The sensitivity analysis includes varying the injection and extraction rates, permeability field characteristics, and the amount and distribution of NAPL, etc. The results from these sensitivity studies are then used to determine the duration of the tracer test, the mass of each tracer needed, the injection and extraction rates, the extraction well effluent tracer concentrations over time and the cumulative amount of tracer recoverable at the end of the tracer test. A preliminary design for the PITT operation is then chosen based upon the results of these sensitivity studies. The validity of the preliminary design is then tested in the field, before the PITT, by conducting a conservative interwell tracer test (CITT) which uses one or more non-partitioning tracers. The CITT is a relatively short-term test that is used to fine-tune the final PITT design to ensure that a successful PITT will be conducted.

The main objectives of the CITT are to:

- Determine the percent recoveries of the tracer at each well
- Determine the actual residence times of the tracers in the subsurface
- Determine the actual swept pore volume to finalize the PITT design
- Determine the effective permeability of the aquifer
- Obtain insights into the relative heterogeneity of the aquifer and a better understanding of the subsurface flow system
- Act as a shakedown for the ensuing PITT in terms of equipment setup, sample collection, well monitoring, etc.

Based on the objectives of the CITT, it is evident that the model predictions for the CITT do not need to be precise. The information gained from the CITT is of great value in making final decisions on the PITT design. CITT results are used to update and calibrate the geosystem model. Then, a number of numerical simulations, for sensitivity analysis, are conducted to study the behavior of different partitioning tracers in order to formulate an optimum final design for the PITT. The results of these post-CITT sensitivity analyses are then used to:

- Finalize the selection of the tracers
- Determine the duration of the PITT
- Determine the mass of each tracer needed
- Determine the injection and extraction rates
- Determine sampling frequency at monitor and extraction wells
- Predict the swept volume
- Predict the extraction well effluent tracer concentrations
- Predict the amount of tracer recovered by the end of the tracer test

8.2 Simulation Model Development

8.2.1 Well-Field Configuration

Preliminary UTCHEM simulations based on site hydrogeological data, indicated that the PITT well field would be most efficiently configured with a divergent line-drive geometry, i.e., a line of injection wells flanked on both sides by lines of extraction wells. In order to maintain hydraulic control and to ensure that an adequate portion of the well field will be swept, each injection or extraction well is spaced 10 ft from its nearest neighbor within a line of injection or extraction wells. The interwell distance between any pair of injection and extraction wells is 15 ft. This corresponds to a well-field size of 20 ft by 30 ft. The well-field configuration is shown schematically in Figure 4.1. As the figure shows, the well field consists of 11 wells. There are six extractors and three injectors. In addition, a hydraulic control well is located outside the well field on each end of the line of injection wells. These two wells are used only as hydraulic control wells (i.e., only water will be injected into these wells during flooding operations) to provide hydraulic containment of the tracer flowpaths between injection and extraction wells. Tracer injection at the center of the well-field panel, with simultaneous extraction on both sides of the well-field array, drives the tracer injectate divergently outward towards the extraction wells where tracer recovery occurs.

8.2.2 Simulation Domain

The plan view of the three-dimensional UTCHEM model grid is illustrated in Figure 8.1. The figure also shows the locations of the injection wells, the extraction wells, and the elevation contours defining the top of the clay aquitard. The aquifer volume in the test zone was simulated using a three-dimensional 25 X 25 X 16 mesh consisting of a total of 10,000 grid blocks. The horizontal extent of the model was 141 ft long, and 99 ft wide. The vertical extent of the model was 13 ft thick to represent the saturated thickness of the test zone, and corresponds to a bottom elevation of about 5 ft amsl, and a top elevation of 18 ft amsl. This overall vertical thickness of 13 ft was divided into 16 layers with a uniform thickness of 0.5 ft per layer for the bottom 12 layers. The clay elevation contour of the aquitard was incorporated into the model by mapping all grid cells with centroid locations below the surface of the aquitard (as defined by the kriged elevations shown in Figure 8.1 as clay blocks), effectively making them no-flow boundaries. The simulation dimensions and the number of gridblocks were chosen to minimize boundary effects. No-flow boundary conditions were assumed for the top of the simulation domain. The pressures at two outer boundaries were kept constant to establish a regional hydraulic gradient of 0.015.

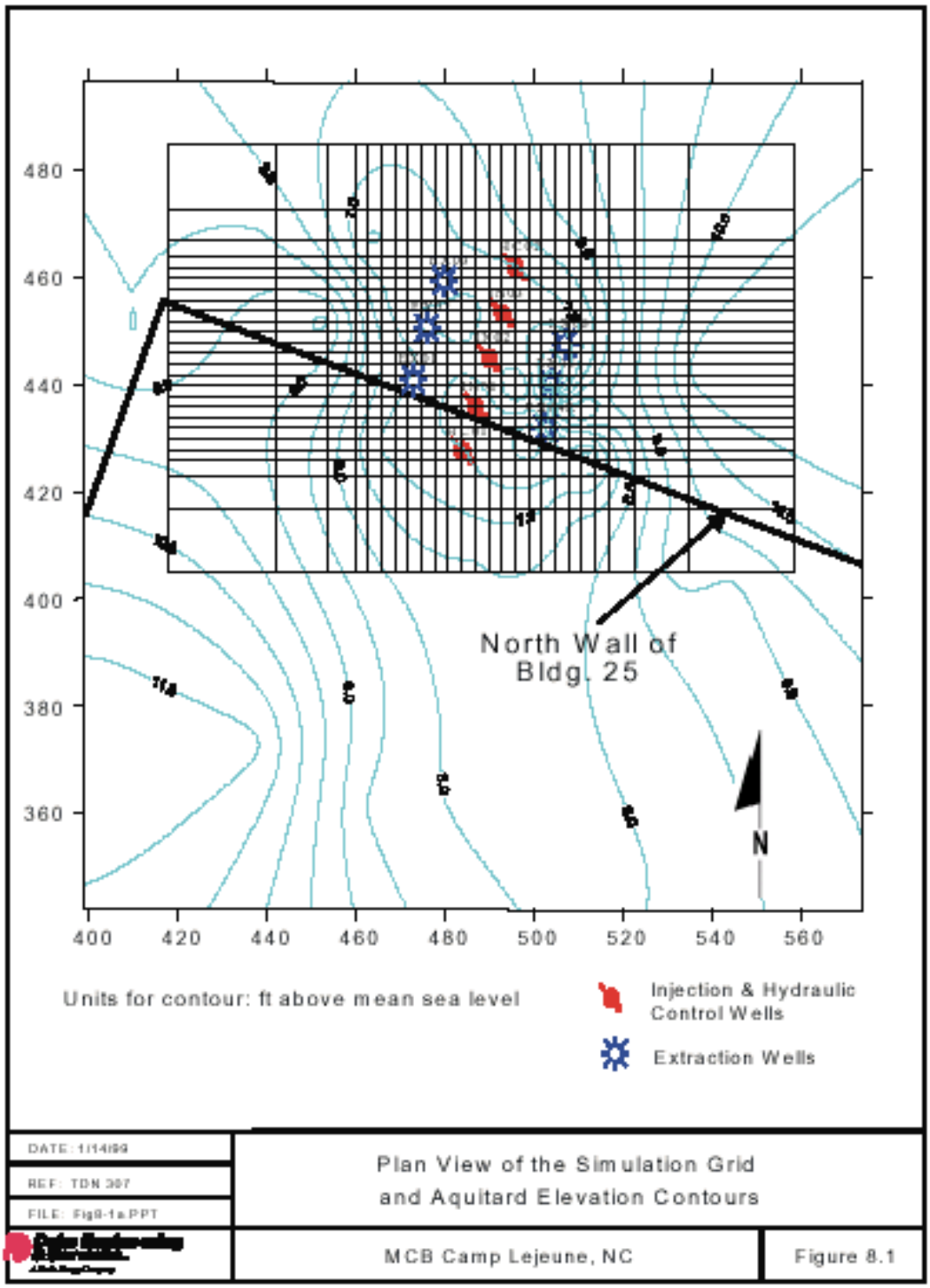

Figure 8.1. Plan View of the Simulation Grid and Aquitard Elevation Contour

8.2.3 Physical Properties of Porous Media and Fluids

The porous media and fluid physical properties used in our model were based upon data from the site investigations or from similar geosystems by analogy. The values for some of the properties are provided below.

porosity	0.34
average permeability	0.4 darcies
density of water	1 g/cm^3
density of NAPL	1.63 g/cm^3
water-NAPL interfacial tension	45 dynes/cm
NAPL viscosity	0.89 cp
water viscosity	1.0 cp

Values for relative permeability and capillary functions were taken from the literature based on data from similar sites. It should be noted, however, relative permeability and capillary functions are not very important parameters for the PITT since the process is essentially single-phase flow with the second phase as residual NAPL. The capillary pressure equals zero in this case. The initial NAPL saturation distribution was based on the soil sampling analytical data. A NAPL saturation of 10% for the bottom two feet of the aquifer was used for the simulations. Observations of soil cores also indicated that the permeability at the bottom portion of the shallow aquifer is significantly lower than the main portion of the aquifer, as discussed in Section 5.0. This vertical heterogeneity was addressed in the model by assigning a permeability contrast of 2 between the upper intervals versus the bottom portion of the model.

The tracers used for the simulations are based on the laboratory column experiments. The tracers and their measured partition coefficients are listed in Table 8.1.

Table 8.1 Tracers and their Partition Coefficients

Tracer Name	Partition Coefficient
1-Propanol	0
4-Methyl-2-Pentanol	4
1-Hexanol	8
1-Heptanol	35

8.3 CITT Design

As discussed in Section 8.1, a number of sensitivity analyses were run to simulate the performance of the tracer test in order to provide an optimum design for the PITT. The sensitivity analyses included varying the injection and extraction rates and permeability distribution, etc. The results generated from these simulations were used to design the CITT. Tables 8.2 and 8.5 summarize the pertinent CITT design variables. The predicted tracer response curve for a conservative tracer at each of the extraction wells is shown in Figure 8.2. The simulation predictions, in terms of swept pore volume, the percentage of tracer recovered, and the tracer residence times for each extraction well, are given in Table 8.6. The predicted tracer recovery was approximately 90%. The predicted swept aquifer pore volume was approximately 4,920 gallons after 14 days of tracer operation. The actual results, including the predicted tracer response curves at each well, may vary somewhat for a variety of reasons such as the uncertainty in the aquifer permeability field, i.e., heterogeneity. However, the CITT can be successful over a wide range of uncertainties since the purpose of the CITT is to obtain an understanding of how an induced-flow system behaves in the test zone site. The CITT data was used to calibrate the numerical model for the final PITT design simulations.

Table 8.2 Design Summary of CITT Flow Rates

Well Type	Well Name	Flow Rate (gpm)	Total (gpm)
Extraction	EX1	0.25	1.5
	EX2	0.25	
	EX3	0.25	
	EX4R	0.25	
	EX5	0.25	
	EX6	0.25	
Injection	IN1	0.2	1.2
	IN2	0.2	
	IN3	0.2	
Hydraulic Control	HC1	0.3	
	HC2	0.3	

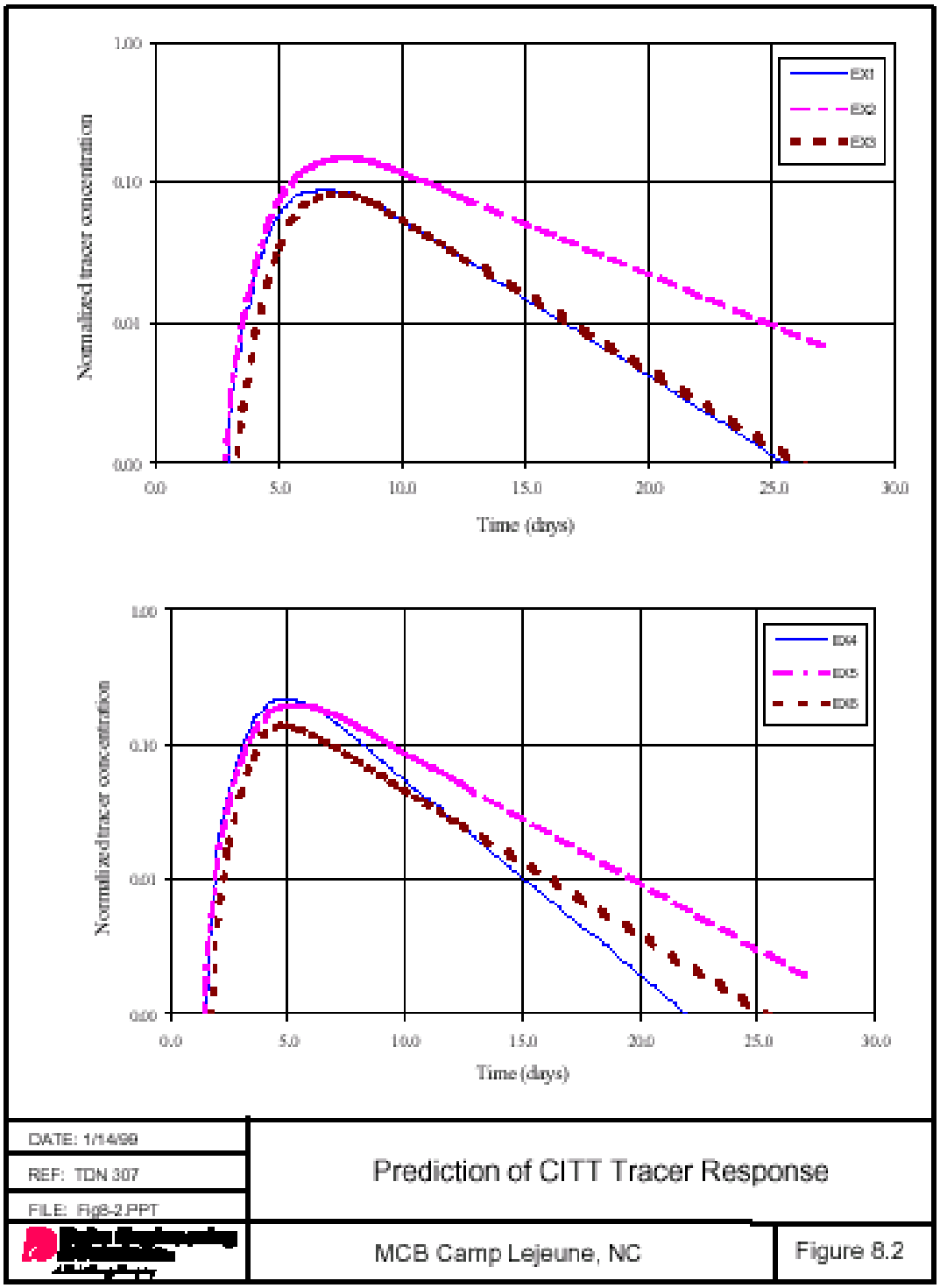

Figure 8.2. Prediction of CITT Tracer Response

Table 8.3 Design Summary of CITT Phases

Injectate		Duration (Days)	Cumulative Time (Days)
IN1, IN2, IN3	*HC1,HC2*		
Water	Water	1	1
Tracer + Water	Water	2.5	3.5
Water	Water	11.5	15

Table 8.4 Summary of Tracer Injection Operation

Tracer	Slug Size (gals)	Total Mass (kg)	Injectate Concentration (mg/L)
Potassium Bromide	2,160	12	1,000 (as bromide)

Table 8.5 Sampling Schedule for the CITT

Sample Type	Day (since water injection began)	Day (since tracer injection began)	Sampling frequency (hours per sample)	Number of samples per well or sample point	Total number of samples
Extraction Well	1	0	0	0	0
	2-4	1-3	12	6	36
	5-8	4-7	6	16	96
	9-13	8-12	12	10	60
	14-15	13-14	24	2	12
Sub-total					**204**
Injectate	1	0	0	0	0
	2-4	1-3	6	12	12
	5-15	4-14	0	0	0
Sub-total					**12**
Total					**216**
Total (after adding additional 5% of samples for duplicates and QA/QC)					**227**

Table 8.6 Summary of CITT Simulation Predictions

Well Name	Tracer Recovery (%)	Swept Volume (gals)	Mean Tracer Residence Time (days)
EX1	10	570	7.0
EX2	19	1,230	7.7
EX3	7	460	7.4
EX4	20	920	5.3
EX5	23	1,170	6.0
EX6	11	570	5.7
Total	90	4,920	

8.4 PITT Design

As might be anticipated, the actual CITT response curves differed from the model prediction. The detailed CITT results are presented in Section 11.3. A comparison of Table 8.6 and Table 11.1 indicates that the model prediction and the actual results were in good agreement; therefore, the geosystem model was a reasonable representation of the actual aquifer. Nonetheless, the geosystem model was updated with the results of the CITT to further refine the model for the PITT design simulations. The most important adjustment made to the geosystem model for the PITT design was to focus the tracer flowpaths along the bottom portion of the aquifer where the DNAPL resides through the use of a dual injection system. The dual injection design provides vertical hydraulic control of tracer flowpaths, and is described as follows. At each of the three injection wells, clean, tracer-free water was injected into the upper screen only (above an inflatable packer), along with the simultaneous injection of tracers below the packer into the lower screen (see Figures 4.2 and 4.4 for injection well configuration). The dual injection system also prevented tracer flowpaths from moving upwards through the LNAPL (Varsol™) smear zone which coincides with the fluctuating water table (Figure 4.4). If tracer flowpaths were allowed to travel through the LNAPL zone, there would be interference with partitioning of tracers occurring in both the LNAPL and DNAPL zones. This interference between the LNAPL and DNAPL zones would therefore increase the difficulty of analyzing the PITT data in order to obtain meaningful information with respect to the DNAPL zone. Before considering the dual injection scheme, PITT flow rates were designed for overproduction during the PITT, i.e., greater total extraction rates than total injection rates. Overproduction has the potential undesirable effect of declining flow rates over time at the extraction wells (i.e., due to dewatering the test zone). However, the addition of upper-level water injection improved the balance of flow between total injection rates and total extraction rates, and minimized the potential for dewatering at extraction wells during the PITT operation.

As in the design of the CITT, sensitivity simulations were conducted to provide an optimum design for the PITT. Tables 8.7 through 8.10 summarize the pertinent design variables for the PITT, based upon the calibrated geosystem model and the sensitivity studies. The predicted tracer response curves for all of the extraction wells are shown in Figures 8.3 through 8.5. The simulation predictions are summarized in Table 8.11 for swept pore volume, percentage of tracer recovered, and the interwell residence times (i.e., tracer travel time between an injection and extraction well pair).

Based on the results of multiple sensitivity simulations, the predicted tracer recovery at the end of the PITT was expected to be approximately 93% to 96%. The predicted swept aquifer pore volume, based on the simulated tracer response analysis, was approximately 6,450 gallons. The actual PITT results varied for a number of reasons, including the uncertainties in the degree of aquifer heterogeneity and the distribution of DNAPL in the swept pore volume. This is discussed in further detail in Section 11.4.

Table 8.7 Design Summary of PITT Flow Rate

Well Type	Well Name	Flow Rate (gpm)	Total (gpm)
Extraction	EX1	0.25	1.55
	EX2	0.25	
	EX3	0.30	
	EX4	0.25	
	EX5	0.25	
	EX6	0.25	
Injection	IN1-lower	0.2	1.44
	IN2-lower	0.2	
	IN3-lower	0.2	
	IN1-upper	0.08	
	IN2-upper	0.08	
	IN3-upper	0.08	
Hydraulic Control	HC1	0.3	
	HC2	0.3	

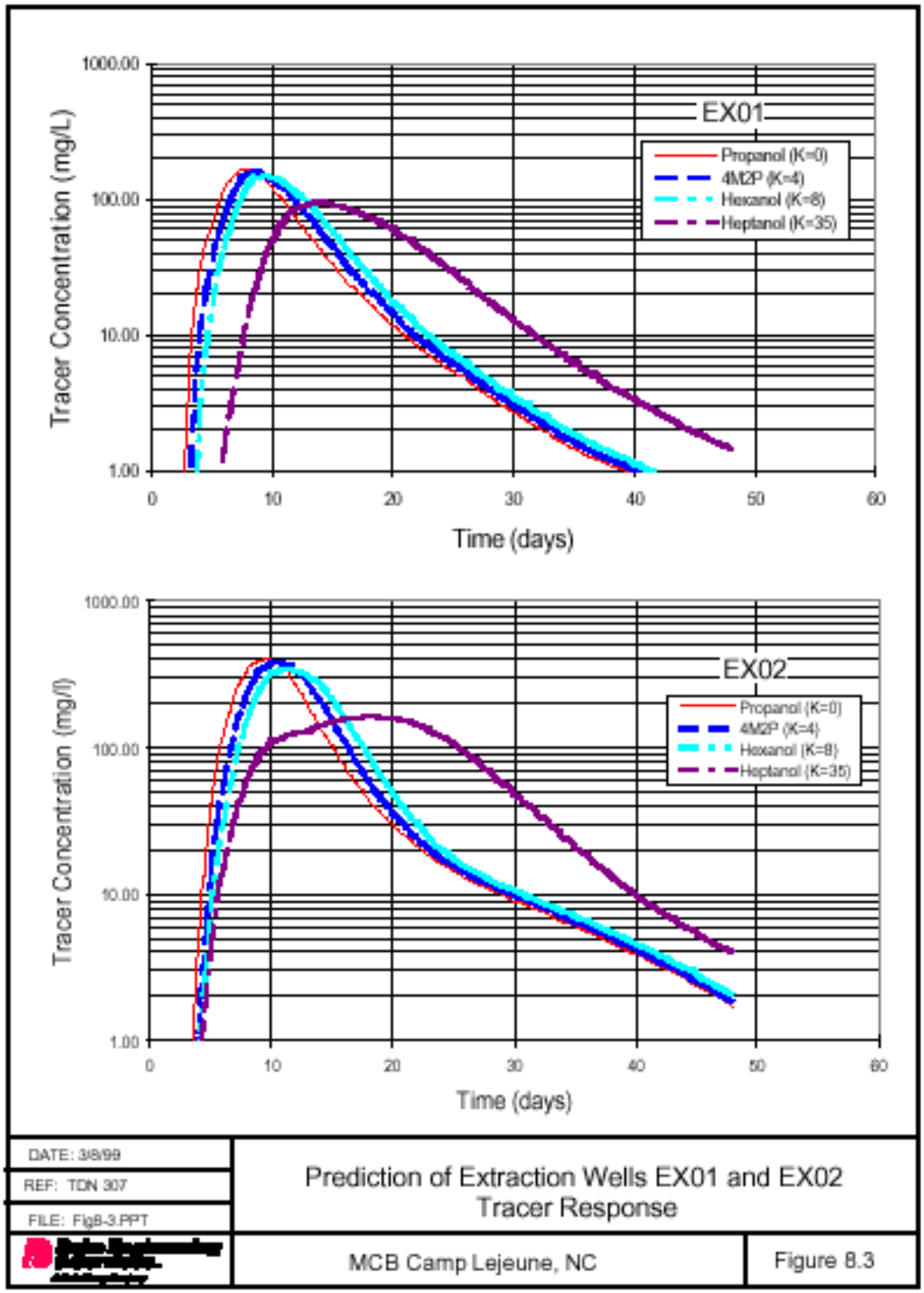

Figure 8.3. Prediction of Extraction Wells EX01 and EX02 Tracer Response

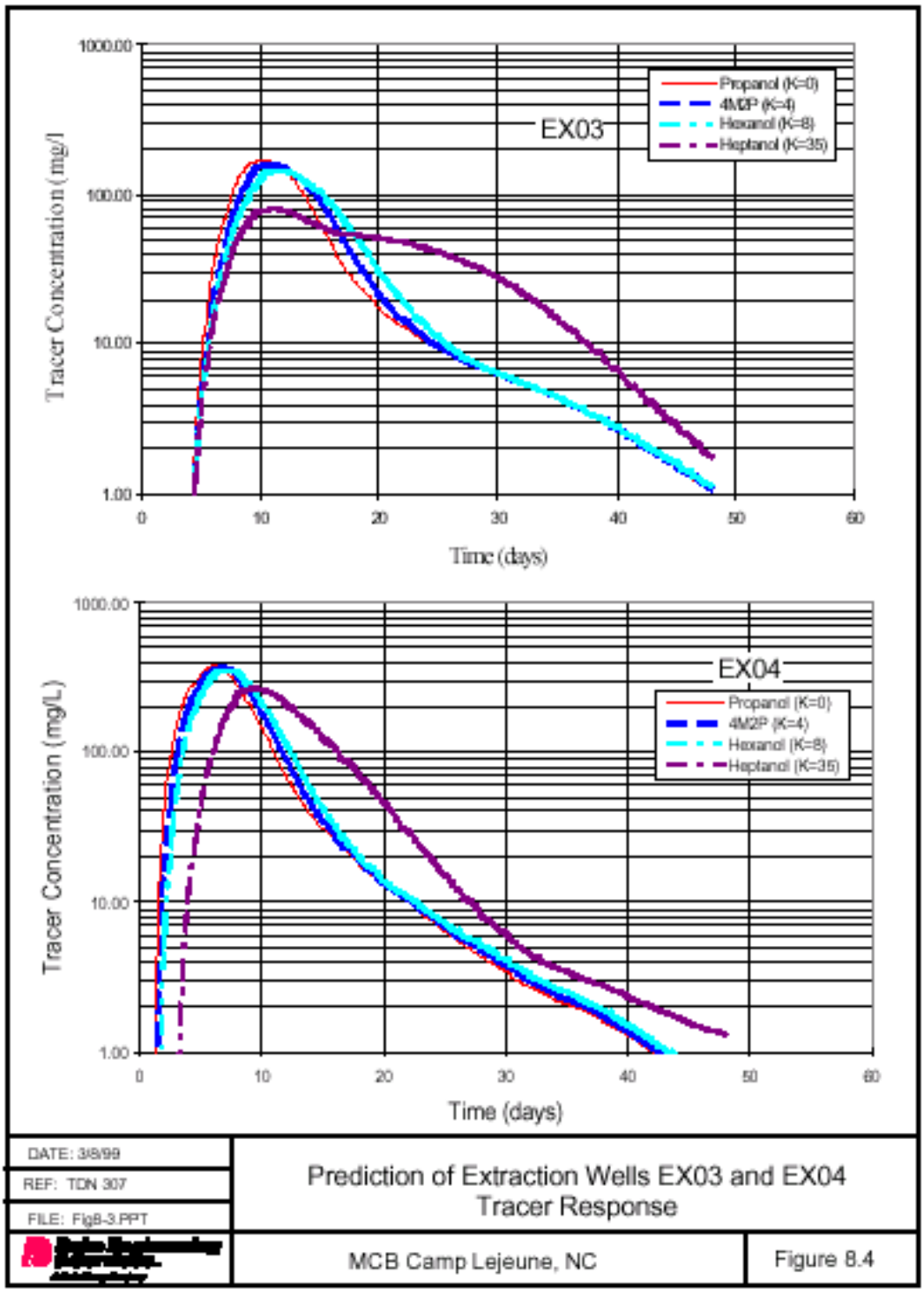

Figure 8.4. Prediction of Extraction Wells EX03 and EX04 Tracer Response

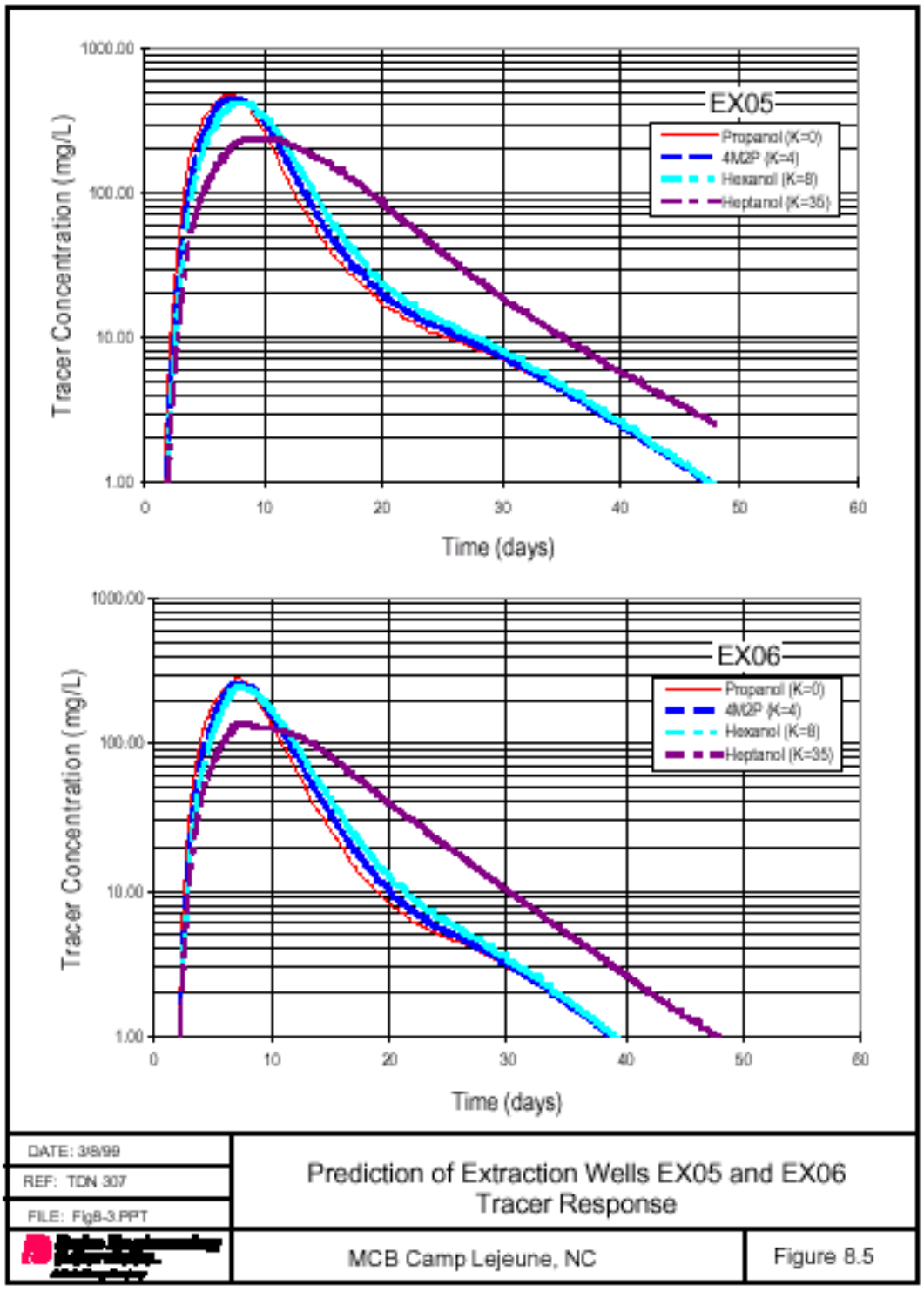

Figure 8.5. Prediction of Extraction Wells EX05 and EX06 Tracer Response

Table 8.8 Design Summary of PITT Operation Phases

Injectate		Duration (Days)	Cumulative Time (Days)
IN1, IN2, IN3	*HC1,HC2, IN1-upper, IN2-upper, IN3-upper*		
Water	Water	1	1
Tracer + Water	Water	5.8	6.8
Water	Water	34.2	41

Table 8.9 Summary of Tracer Injection Operation

Tracer Name	Partition Coefficient	Total Mass (kg)	Injectate Concentration (mg/L)
1-Propanol	0	19	1,000
Methanol	0	19	1,000
4-Methyl-2-Pentanol	4	19	1,000
1-Hexanol	8	19	1,000
1-Heptanol	35	13	700

Table 8.10 Sampling Schedule for the PITT

Sample Type	Day (since water injection began)	Day (since tracer injection began)	Sampling Frequency (hour per sample)	Number of Samples per Well or Sample Point	Total Number of Samples
Extraction Well	1	0	0	0	0
	2-7	1-6	6	24	144
	8-13	7-12	12	12	72
	14-41	13-40	24	28	168
Multilevel Sampler (only three out of nine sample ports were functioning during the PITT)	1	0	0	0	0
	2-7	1-6	8	18	54
	8-13	7-12	12	12	36
	14-41	13-40	24	28	84
Total Extraction Well and Multilevel Sampler Samples					558
Injectate	1	0	0	0	0
	2-7	1-6	6	24	24
	8-41	7-40	0	0	0
Total Injectate Samples					24
Sub-Total					582
Total (after adding additional 20% of samples for duplicates and QA/QC)					700

Table 8.11 Summary of PITT Simulation Predictions

Well Name	Tracer Recovery (%)	Swept Volume (gals)	Mean Residence Time (days)
EX1	9	660	8
EX2	22	1,800	9
EX3	10	940	10
EX4R	18	920	6
EX5	24	1,400	7
EX6	13	730	6
Total	96	6,450	

9.0 CONSERVATIVE INTERWELL TRACER TEST (CITT)

This section provides the operational details and test results for the conservative interwell tracer test (CITT) performed during April 15–28, 1998, using design flow rates obtained from preliminary UTCHEM modeling. The objectives of this test were to determine the average subsurface tracer residence times, tracer swept pore volumes for each of the interwell pairs, and as otherwise discussed in Section 8.1 (PITT Design Strategy and Modeling Approach). These results were then used to update the UTCHEM model for the final PITT design simulations. A general layout of the test system is shown in Figure 9.1. Tracer and water-flood solutions were mixed in the storage tanks and then injected into the aquifer via the autocollector/control trailer. Packers were installed in the injection and hydraulic control wells for the purpose of separating the upper and lower screens. The tracer injection line was run through the packer to direct flow through the lower screen into the lower zone of the shallow aquifer. Injectate flowing to the extraction wells was then pumped from the wells to the waste tanker via the autocollector/control trailer.

The purpose of autocollector trailer and the data acquisition system (DAS) was to collect samples, control and log injection flow rates and monitor water levels. Flow rate and water level data was electronically recorded once every 20 minutes.

Injection flow rates were manually measured daily using a stopwatch and graduated cylinder. Each manual measurement was compared to the DAS-recorded flow rate. If the flow rate varied by more than 10%, the appropriate electronic flow meter was recalibrated. Extraction well flow rates were not monitored with conventional flow meters because the pneumatic pumps provide a pulsed flow. The flow rates in the extraction wells, therefore, were determined by monitoring flow totalizers and elapsed time.

Water levels in the extraction wells and lower zones of the injection wells were electronically measured and recorded by the DAS. Manual measurements taken with a water level meter were compared to the DAS data; if significant deviations were observed, then corrective action was taken (e.g. replacement or recalibration of transducers) to correct the discrepancies Water levels were also measured in the upper zones of the hydraulic control wells and injection wells and in selected monitor wells.

On April 14, 1998 a CITT was initiated and conducted in the following sequence:

1. pre-injection water flood,
2. conservative tracer injection, and
3. post-injection water flood.

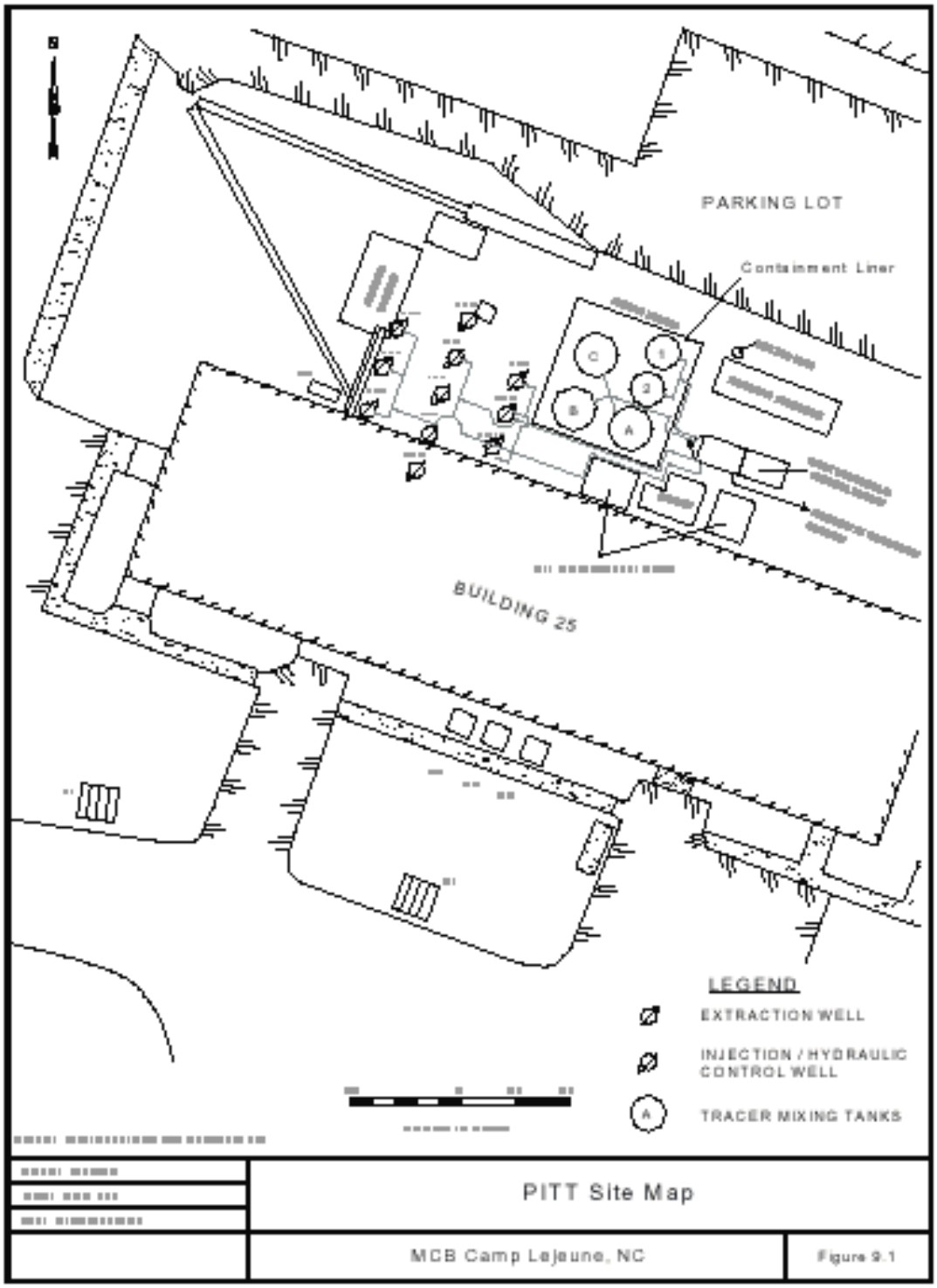

Figure 9.1. PITT Site Map

The pre-injection water flood started 24 hours before tracer injection to establish a steady-state flow regime in the well field. A tracer slug of approximately 2,100 gallons of approximately 970 mg/L of bromide ion (Br^-) was injected over a 59-hour period. Tracer injection was followed by 12 days of water flooding to transport the tracer through the zone of interest. These phases were conducted using the design extraction and injection flow rates summarized in Table 8.1. The total CITT duration was about two weeks.

All water injected during the test contained $CaCl_2$ at a concentration of approximately 1,000 mg/L. This was done to decrease the probability of clay particle mobilization due to ion exchange in the aquifer sediments. Mobilization of these fine clay particles could have resulted in significant pore-plugging, thereby reducing the hydraulic conductivity and thus the sustainable flow rates at the injection and extraction wells. Injectate batches were checked with a conductivity probe before injection to ensure that the $CaCl_2$ concentration was within acceptable limits.

Effluent samples were collected manually from each extraction well according to the sampling schedule in Table 8.5, and analyzed for Br^- concentration. Concentrations were measured using an Orion Model 9435BN bromide selective electrode and model 900200 double junction reference electrode connected to an Orion Model 250A pH meter. The analysis was carried out using the DE&S standard operating procedure outlined in Appendix L.

The Br^- tracer concentration histories are plotted in Figure 9.2 to show the tracer response at the six extraction wells. The Br^- tracer response data was then normalized (to the Br^- injectate concentration) for the CITT data analysis. The normalized tracer response data and their corresponding fitted curves, (based on Equation 11.2-2 in Section 11.3) are shown in Figures 9.3a to 9.3c for the six extraction wells. The tracer curves were analyzed using the method of temporal moments (which is discussed in Section 11.1; PITT Data Analysis). The resulting estimates of the tracer recovery, swept volume, and mean residence time for each well are summarized in Table 11.1. The total aquifer pore volume swept by the tracers was approximately 4,810 gallons as determined by adding up the swept volumes calculated for each well.

Based upon the results from the CITT, the geosystem model used was then calibrated to reflect more closely the actual test domain and was used to design the PITT as described in Section 8.4.

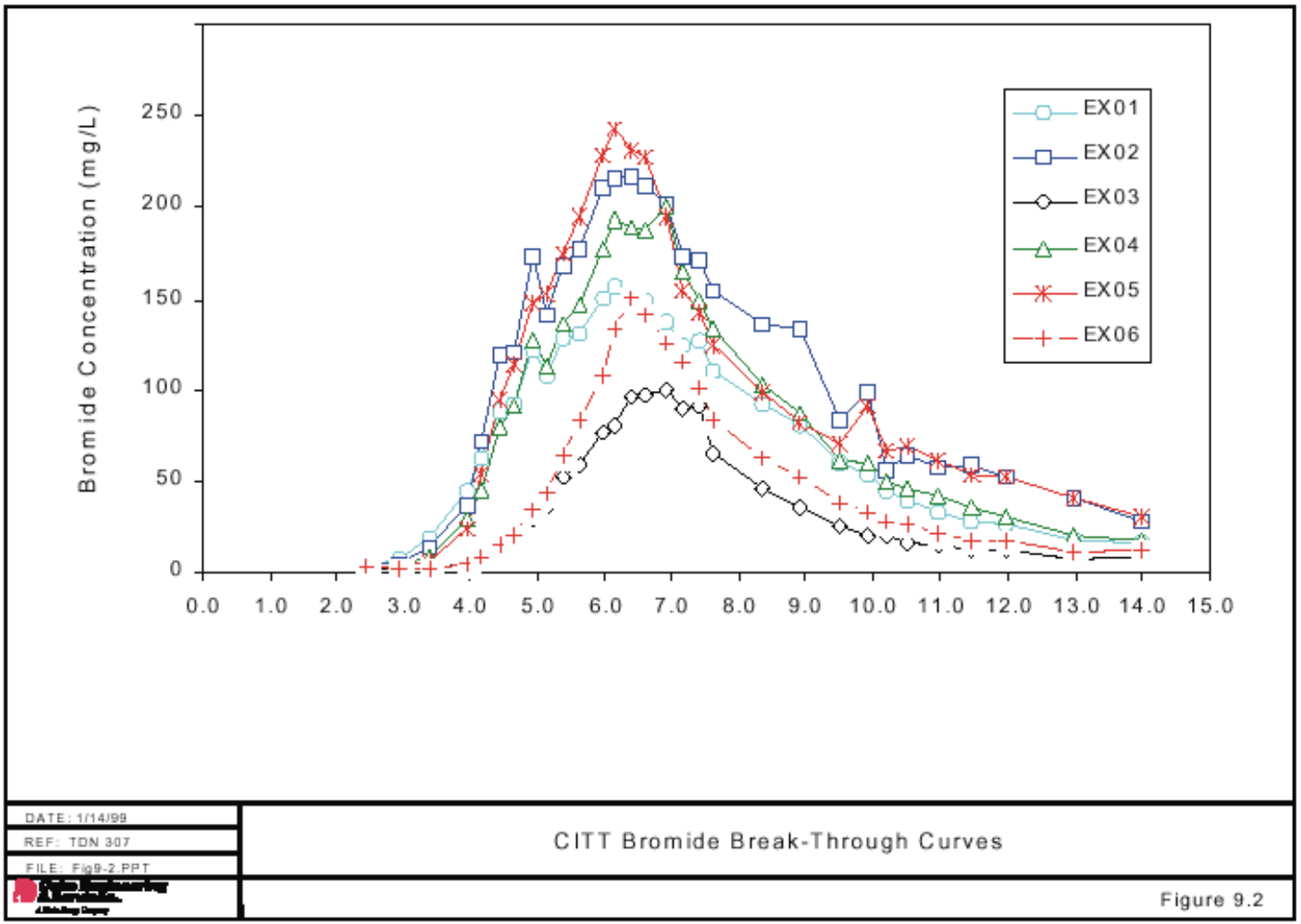

Figure 9.2. CITT Bromide Break-Through Curves

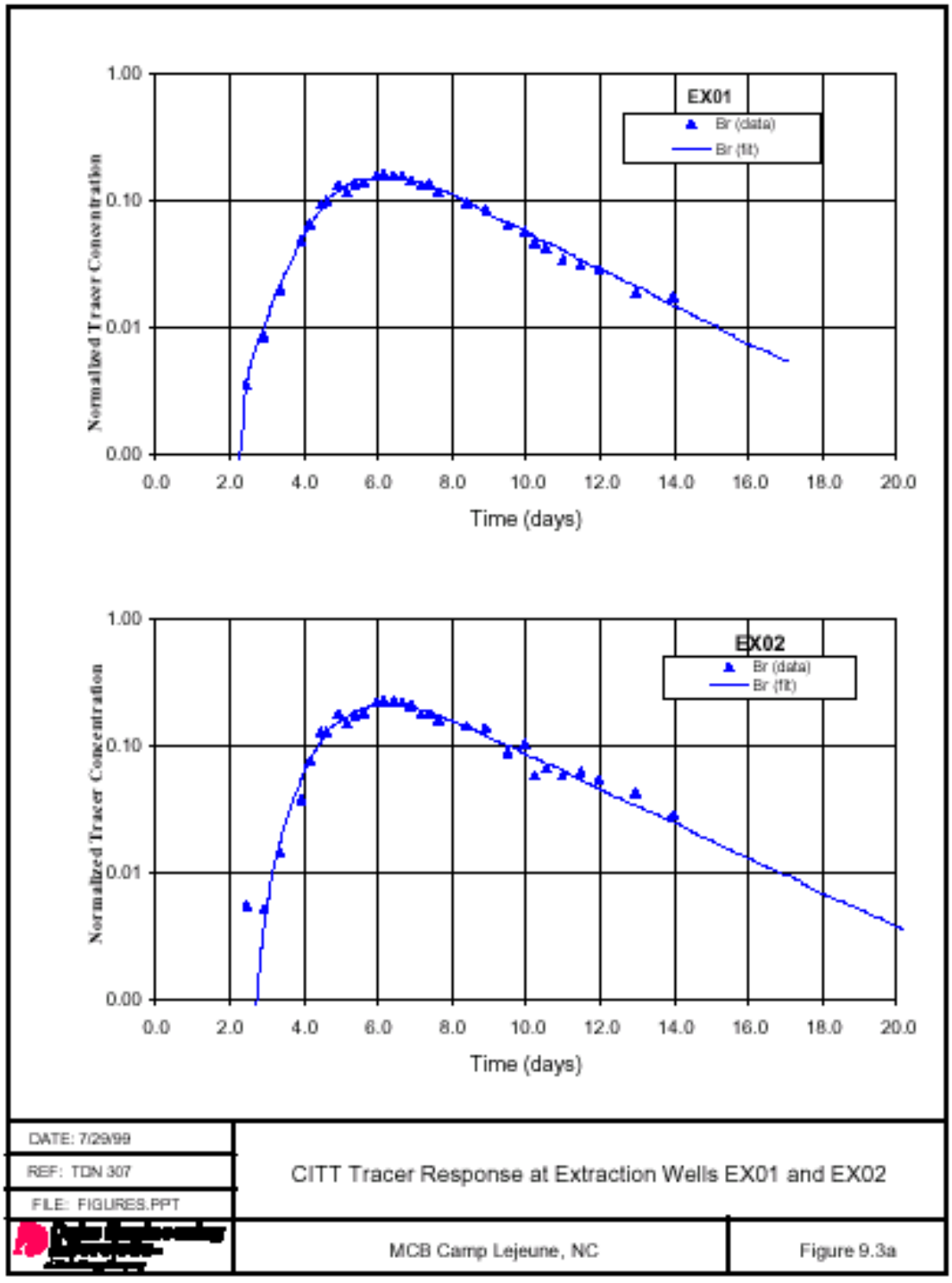

Figure 9.3a. CITT Tracer Response at Extraction Wells EX01 and EX02

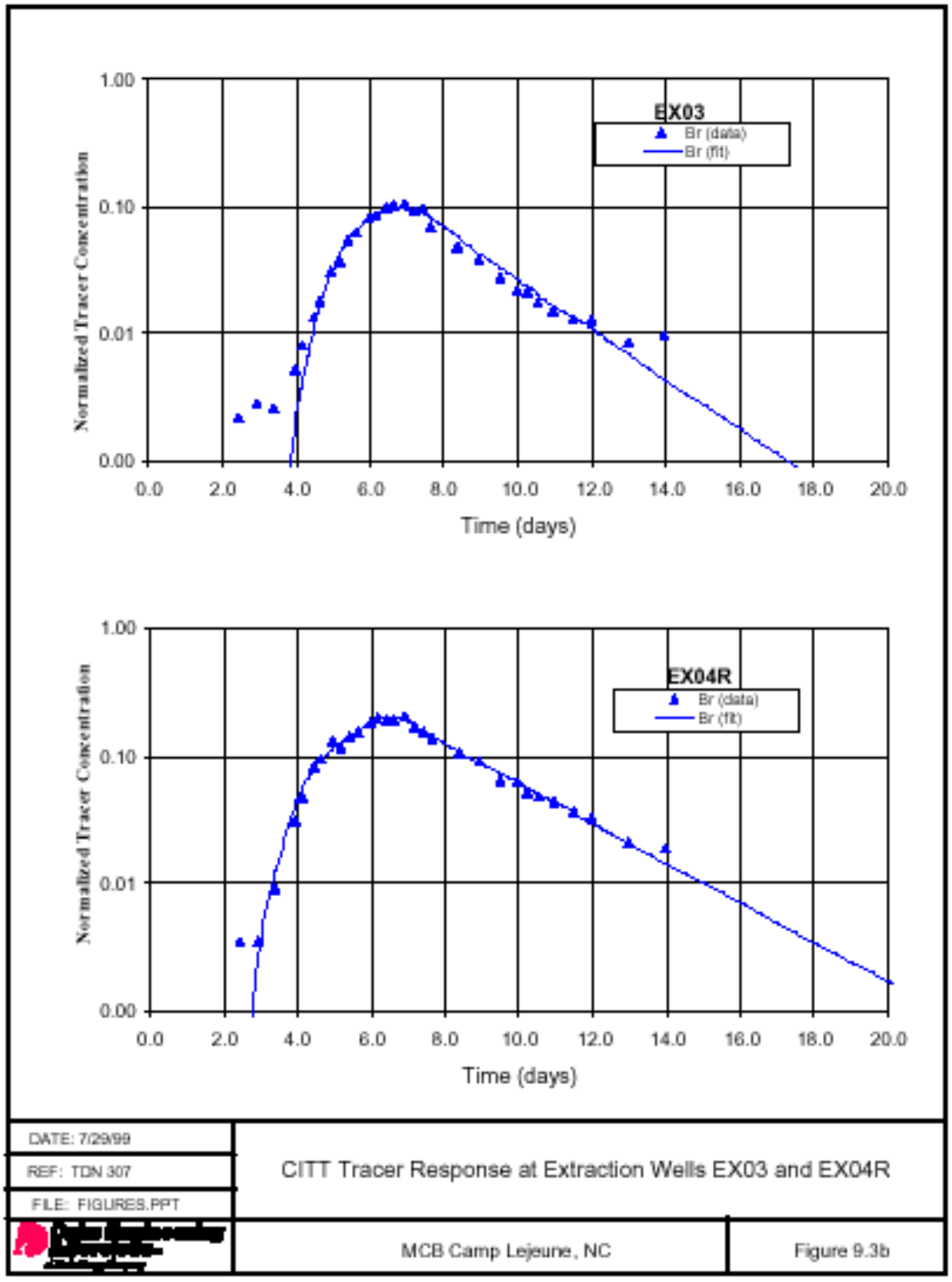

Figure 9.3b. CITT Tracer Response at Extraction Wells EX03 and EX04R

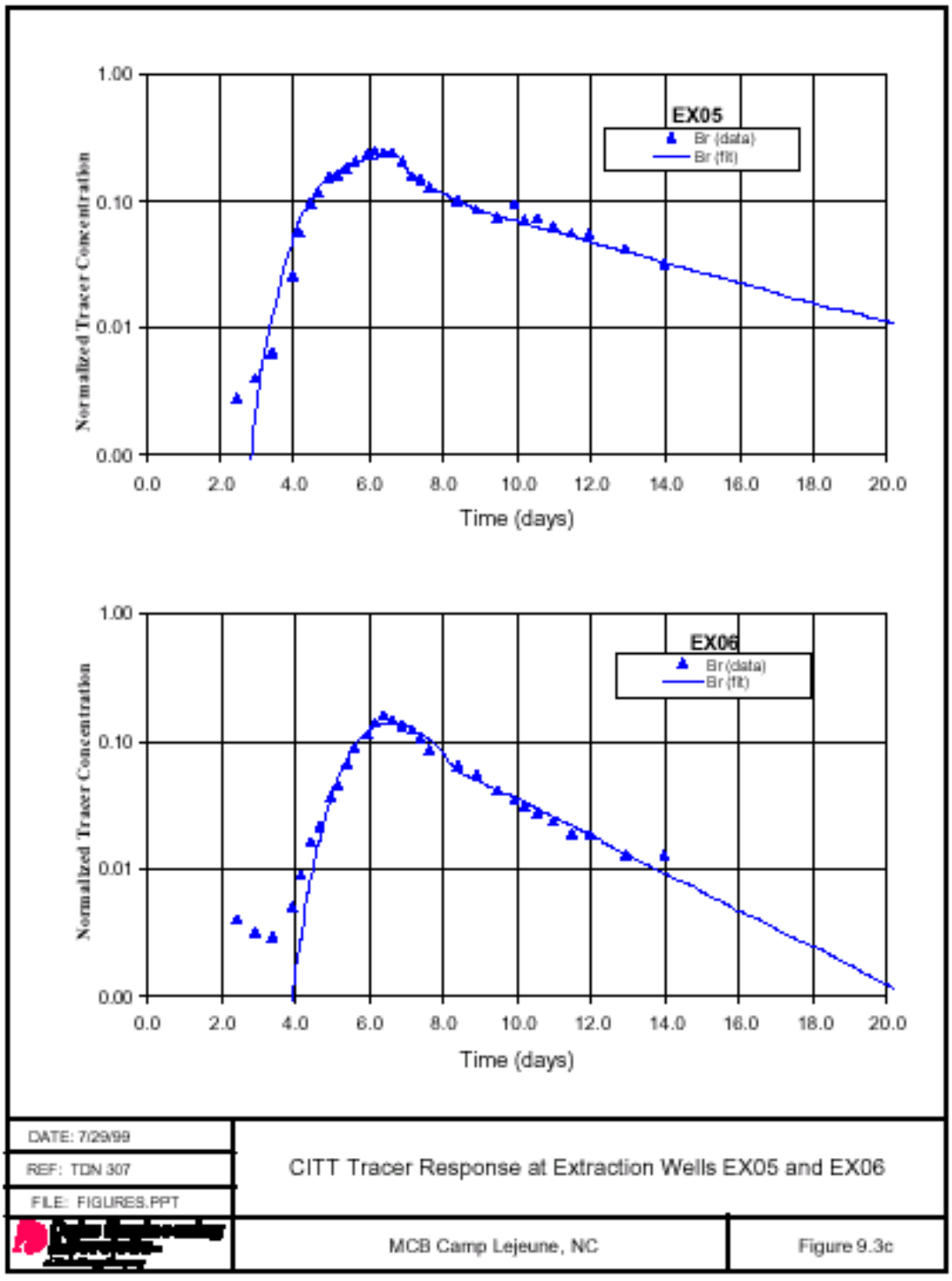

Figure 9.3c. CITT Tracer Response at Extraction Wells EX05 and EX06

Table 9.1 Summary of CITT Results

Well Name	Tracer Recovery (%)	Swept Volume (gallons)	Mean Residence Time (days)
EX1	14.5	800	6.4
EX2	20.8	1,230	6.8
EX3	6.7	390	6.6
EX4R	16	910	6.5
EX5	16	1,000	7.3
EX6	8.	480	6.9
Total	82.0	4,810	

To minimize the movement of tracers vertically upward towards the water table and the associated LNAPL smear zone, a dual injection system was recommended and implemented for the PITT. In addition, the extraction rates were also slightly adjusted to balance the uneven tracer mass recovery observed in the CITT. The PITT results, as presented in Section 11.0, support the conclusion that the information gained from the CITT was of great value in making final decisions on the PITT design.

10.0 PITT FIELD IMPLEMENTATION

This section provides an overview of the actual field implementation of the PITT. Included in the discussion is a chronological description of the main events involved in the conduct of the test and the main sampling events. A more detailed description of the actual field activities and sampling events can be found in the Work Plan and the Sampling and Analysis Plan (DE&S 1998a; DE&S 1998b).

The test system was shut down after completion of the CITT to perform general maintenance, install system upgrades, and make modifications to accommodate the recommendations for the final PITT design. The final PITT design required that three additional injection lines be added to facilitate upper hydraulic-control injection into the upper screen intervals of the three IN wells. Injection of tracer-free water into the upper zone was intended to keep the tracers from flowing through the Varsol™ NAPL zone by maintaining hydraulic control of the upper section of the aquifer.

10.1 PITT Operations

The tracer solution, which contained both non-partitioning and partitioning tracers, was prepared by filling 3,000 gallon tanks with 2,500 gallons of potable water and then adding the tracers in four liter increments. Two tracer batches were mixed in separate tanks resulting in a tracer slug of about 5,000 gallons. Table 10.1 provides a list of the tracers mixed in the batch, the volume added per tank and the approximate final concentrations. The heavier or longer-chained alcohols, such as heptanol, have low aqueous solubilities and therefore, do not readily mix with water. After adding the alcohols to the tank, an alcohol phase was clearly seen floating on top of the water. The alcohols were completely mixed into solution by recirculating the water in the tanks until there was no visible evidence of an undissolved alcohol phase. Mixing was considered complete after approximately two days of recirculation.

Table 10.1 Tracer Volumes and Approximate Concentrations per Tank

Tracer	Volume added/Tank	Concentration (mg/L)
1-Propanol	12 liters	1,000
Methanol	3 gallons	950
4-methyl-2-Pentanol	12 liters	1,000
1-Hexanol	12 liters	1,000
1-Heptanol	8 liters	700

To avoid tracer concentration fluctuations in the injectate it is important that the tracer batch be completely homogenous. To achieve this, the tanks were cross-mixed after the alcohols had been dissolved into solution. Cross mixing was accomplished by inserting the "Tank A" recirculation line into "Tank B" and placing the "Tank B" recirculation line into "Tank A". The tanks were mixed in this manner for approximately 24 hours.

During the interim period between the completion of the CITT and the start of the PITT, the upper zone injection system was installed and maintenance tasks were completed on the test system. Upon completion of these interim activities, in preparation for the PITT, the test system was brought back on line. A water flood was started using the design flow rates as outlined in Table 8.7 to establish a steady-state flow field before initiating tracer injection. On May 13, 1998 following 24 hours of water flooding, tracer injection was begun. Tracer injection continued for a period of approximately five days, which was then immediately followed by 35 days of water flooding. The total duration of the PITT was 40 days; the test was terminated on June, 22 1998.

During the test, flow rates and water levels were controlled, monitored and logged as described in Section 9.0 regarding CITT operations. In addition, during the PITT the upper injection zone system was also electronically controlled by the DAS. Plots of flow rates, cumulative volume and water levels are given in Appendix M. These figures show that flow rates and water levels remained stable throughout the duration of the test.

10.2 PITT Tracer Sampling

As part of the PITT procedure, samples of the injectate, extraction-well effluent and from the multilevel samplers (MLS) were collected and analyzed for tracer concentrations. Injectate and extraction-well samples were collected in 22-mL glass jars capped with Teflon-lined caps. MLS samples were collected in 5-mL vials, also with Teflon-lined caps. All samples were stored in a refrigerator at 4^{o}C.

Injectate samples were taken at various times during tracer injection to verify homogeneity of the tracer slug. An injectate sample was taken 15 minutes before and 15 minutes after tracer injection had begun. The injectate was then sampled at a rate of one sample per day until injection ended. Finally, samples were collected five minutes before injection terminated, and also five and 20 minutes after injection terminated. Samples were taken from a sampling port that had been installed in the injection line.

Effluent samples were collected by the autocollector following the sample schedule outlined in Table 8.10. Manual samples were also taken as backup samples at one half

the automated sampling rate. Duplicates and equipment blanks were taken at a rate of one for every 20 samples collected.

Obtaining sufficient flow from the multilevel sampling points proved to be problematic. After repeated sampling attempts, flow could only be established in three of the nine sampling ports - specifically, MLS-2 at 17.0 ft and 18.5 ft bgs, and MLS-3 at 17.5 ft bgs. Samples were collected at these points following the schedule outlined in Table 8.10.

Samples to be analyzed for tracer concentrations were packed in coolers with ice and shipped to Mantech Environmental of Ada, Oklahoma. A trip blank prepared with diagnostic-grade water was placed in each cooler.

10.3 PITT Tracer Analysis

The PITT samples were analyzed for tracers by a gas chromatography (GC) method which initially involved direct injection onto a capillary column. *The Standard Operating Procedure (SOP) for GC Analysis of Alcohol Compounds in Water Samples*, by Mantech is in Appendix O. However, this very quickly created severe fouling of the capillary column, which is most likely attributed to the calcium content of the samples from $CaCl_2$ injection with the tracers. After several attempts to salvage this method by regenerating the capillary column and even by replacing it, the method was abandoned. Several options were explored, including a full evaporation GC technique that would not involve direct injection and also a high pressure liquid chromatography (HPLC) method. Finally it was decided to switch to direct injection onto a packed column. This method was successful, and was used on all samples analyzed after May 28, 1998, which approximately corresponds to PITT samples collected after May 17, 1998 (four days after the PITT was initiated). No more fouling difficulties were encountered with the use of the packed column; however, the new method raised the tracer detection limits from 1 ppm to 5 ppm for all tracers except for 1-heptanol, which could only be quantified accurately to 10 ppm with the packed column. The time spent exploring alternative analytical methods and developing the packed column method also created a backlog of samples to be analyzed (see Section 11.1.1 for more details). Full details of the analytical methods used for tracer analyses are provided in Appendix Q.

10.4 Water Quality Monitoring

In addition to the samples collected for tracer analysis, various water quality parameters were also monitored as part of the PITT operations. Also, temperature, pH and conductivity were measured at many locations in the well field for input requirements to the SEAR design process.

A small amount of arsenic (≅ 3mg/kg) contamination was present in the dry, granulated calcium chloride used to make the water-flood solutions. Since $CaCl_2$ was injected at

0.1 wt%, arsenic concentrations in the injected solution did not exceed 3 μg/L. Perimeter monitor wells were sampled and analyzed to detect potential increases in arsenic levels that occurred during the PITT. Monitor wells were also sampled for tracer concentrations to verify that hydraulic control was maintained throughout the test and that tracers did not migrate beyond the confines of the test zone.

Samples were collected from wells IW01, RW01, RW02, RW04 and the six extraction wells for field measurement of pH, conductivity, and temperature. The data was used in the design of the surfactant flood and wastewater treatment system. The six extraction wells were sampled two to three times per week and the remaining monitor wells were sampled weekly. The pH was measured with an Orion Model 250A pH meter, and the conductivity and temperature was measured with a conductivity probe. The data for these field-measured parameters are presented in Appendix N.

Extraction well samples were collected from sampling tees in the autocollector trailer. Sample lines were purged before sample collection to prevent cross contamination. Monitor well samples were collected using a peristaltic pump. Samples were taken near the bottom of the well bore and at various depths to determine if any concentration gradients existed in the wells. The data is presented in Appendix N.

Monitor wells MW02 and MW02IW were sampled on a weekly basis and analyzed for the presence of tracers to determine if injectate was escaping from the test zone. In addition, samples were collected from MW02, MW03 and MW05 before, during and after test completion to monitor arsenic levels in the aquifer. The resulting data can be found in Appendix O.

All monitor well samples were collected with a peristaltic pump following the monitor well sampling procedure outlined in Appendix L.

11.0 PITT RESULTS AND DATA ANALYSIS

The field measurements and tracer breakthrough curves collected from the PITT and the significance of these results are discussed in this section. The method of analysis applied to the interpretation of the tracer data is also briefly discussed.

11.1 Laboratory Analytical Results

11.1.1 PITT Samples

As discussed in Section 10.3, all PITT samples were analyzed for tracers by direct injection on a GC. Initially, tracer analysis included methanol, but due to analytical problems, including those discussed below, it was decided to discontinue analyzing for methanol. Since methanol was injected as a backup conservative (i.e., non-partitioning) tracer to 1-propanol, and no difficulties were encountered with analysis of 1-propanol, this has not affected the PITT results. PCE concentrations were also obtained for some PITT samples. The complete PITT data set is included in Appendix O.

Several difficulties were encountered during the analysis of the PITT samples. Already mentioned was fouling of the capillary GC column, which created the need to switch to a packed column to analyze PITT samples collected after day four of the PITT. The SOP for the GC analytical method shown in Appendix O indicates the capillary column had a quantitation limit of approximately 1 ppm whereas the tracers analyzed by packed column had a quantitation limit of approximately 5 ppm. Fouling of the GC column had not been detected during GC method development efforts conducted prior to the PITT. During method development activities, tracer solutions were made up with site ground water and $CaCl_2$, but column fouling was not observed to occur until numerous column injections were made for analysis of the PITT samples. Fouling of the capillary column is most likely attributed to the dissolved $CaCl_2$ that was included in the PITT injectate solution to prevent the mobilization of soil fines in the aquifer. The GC fouling problems created a backlog of samples and resulted in the 7-day sample holding time to be exceeded for as many as 70% of the samples collected during the first 15 days of the PITT. The conventional holding time for VOC samples is seven days without sample preservation and 14 days with sample preservation. When fouling problems came to a head, sample preservation was adopted in the field, on Day 16 of the PITT (May 29, 1998), by adding 1% HCl to all PITT samples to extend the sample holding time to 14 days. Fortunately, the missed sample holding times did not significantly affect the accuracy of the analytical results. Follow-up laboratory studies to evaluate the effect of missed holding time showed that there was no statistically significant difference in the tracer concentrations obtained between samples analyzed within their holding time and

up to two weeks beyond their holding time. A summary of the holding-time study is provided in Appendix P.

A related analytical issue involved quantifying peak tracer concentrations, which sometimes exceeded the maximum tracer detection limit of approximately 200 ppm, and therefore required dilution and reanalysis. Due to the backlog of PITT samples, the reanalysis of such samples was performed three weeks after the initial analysis. In some of these samples, the final analytical result after dilution and reanalysis was ≤ 200 ppm. This decrease in the analytical result for tracer concentrations, between the original sample analysis and the later reanalysis, is suspected to have resulted in an underestimate to some degree of the actual tracer concentrations. The effects of this possible analytical issue on the PITT results are discussed in Section 11.4.3.

Finally, the increase in the quantitation limit to 5-10 ppm, caused by the modification of the analytical method (from a capillary column to a packed column), truncated the useful data set to some degree for all tracers in the tail region of the tracer curve. The effect of this is discussed in Section 11.2.

11.1.2 Monitor Well Samples

Several perimeter monitor wells were sampled for tracers and also for arsenic, during and on completion of the PITT. Wells MW02 and MW02I were sampled for tracer analysis, and wells MW02, MW03, and MW05 were sampled for arsenic analysis. The analytical results for these perimeter monitor points are included at the end of the PITT analytical results in Appendix O.

Most of the tracer analyses in these perimeter monitor wells were below detection limits. In a few of the samples (4 out of 46), tracer was detected at ppm levels, which can be attributed to carryover in the GC column (i.e., carryover from the previous sample analysis) since carryover was also observed in a similar percentage of method blank analyses.

The analytical results for arsenic were below detection limits (<5 ppb) for all of the arsenic monitoring samples.

11.2 Tracer Data Analysis Approach

The first step in the PITT data analysis process was a Quality Assurance/Quality Control (QA/QC) evaluation of the PITT dataset. The QA/QC process is necessary to validate the PITT data for interpretation of the PITT. The PITT data QA/QC report is presented in Appendix O, along with the PITT dataset.

To ensure the quality of the data used for DNAPL volume estimation, tracer data that did not meet QA/QC criteria were eliminated from the data base. The tracer data

QA/QC process also excludes the tracer data in which the measured concentrations are below the detection limits of the GC method of analysis. The reported GC detection limits were about 5 mg/L for all the tracers except 1-heptanol, which was about 10 mg/L. Figure 11.1 provides a visual comparison of the complete tracer dataset (upper plot) versus the tracer data that was used for analysis of the PITT (lower plot). The tracer data for 1-propanol that lie along the detection limit line (upper plot) were not used in the PITT analysis since the concentrations at that point were at the quantitation limit, and we could not have confidence in the accuracy of the data. Therefore, the curve fit for 1-propanol is based upon an extrapolation of the data below the quantitation limit, as shown in the lower plot in Figure 11.1.

The second step of the data analysis process is to evaluate the available field data and select a pair of non-partitioning and partitioning tracers to use for DNAPL volume and saturation estimation. Theoretically, each pair of non-partitioning and partitioning tracer data can give an independent estimate of DNAPL volume and saturation. From a practical standpoint, however, the retardation factor should be greater than 1.2 in order to increase the estimation accuracy (Jin,1995). The conservative tracer used for the PITT data analysis was 1-propanol. As shown in Figure 11.2, the tracer separation between 1-propanol and 4-methyl-2-pentanol (4M2P) is too small to provide an accurate estimate of DNAPL saturation. In general, the retardation factor of 4M2P from this tracer test was smaller compared with 1-hexanol and 1-heptanol. Therefore, the tracer data of 4M2P was not used for the data analysis.

The third step is to fit the tracer response data with smooth curves and estimate the DNAPL volume and saturation as a function of tracer cutoff time. The estimated DNAPL volume and saturation should approach a plateau (not shown, see Jin et al., 1997b, Figure 9) as the tracer test approaches completion. For this tracer test, the analysis was done by fitting the tracer response data using the following exponential decline equation,

$$C(t) = \sum_{i=1}^{n} Exp(a_i + \frac{b_i}{t} + c_i \ln(t)) \qquad (11.2\text{-}1)$$

where n is the number of peaks observed in each individual tracer response curve and a_i, b_i, and c_i are the corresponding fitting parameters. In most cases, there is only one peak in a tracer response curve and the correlation equation (1) can be simplified to

$$C(t) = Exp(a + b/t + c\ln(t)) \qquad (11.2\text{-}2)$$

The fitting of the tracer data to the above equation also provides a unique way of estimating the uncertainty of the estimated DNAPL saturation from a given set of GC measured tracer data. The standard error of DNAPL saturation estimation from a PITT

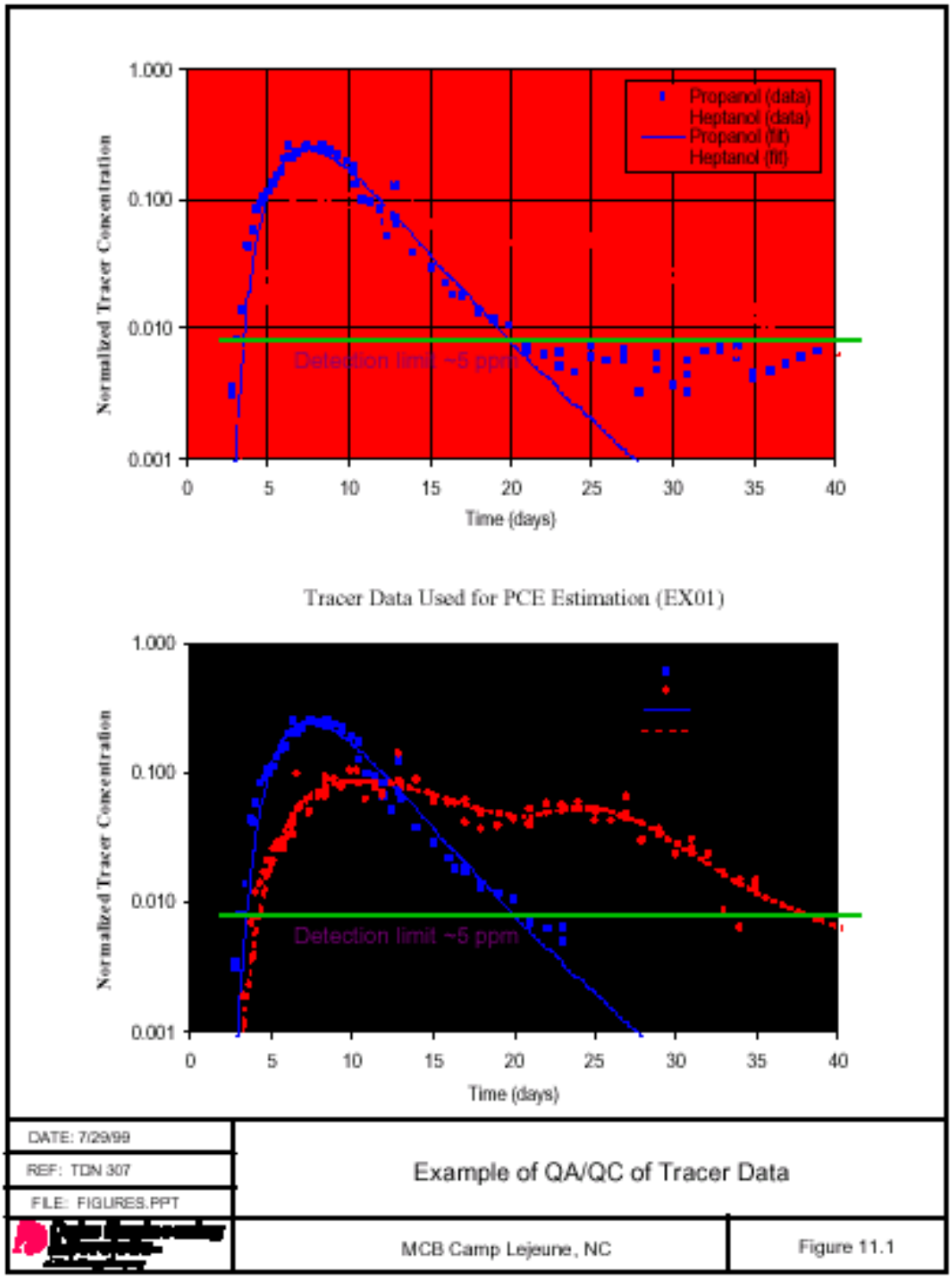

Figure 11.1. Example of QA/QC of Tracer Data

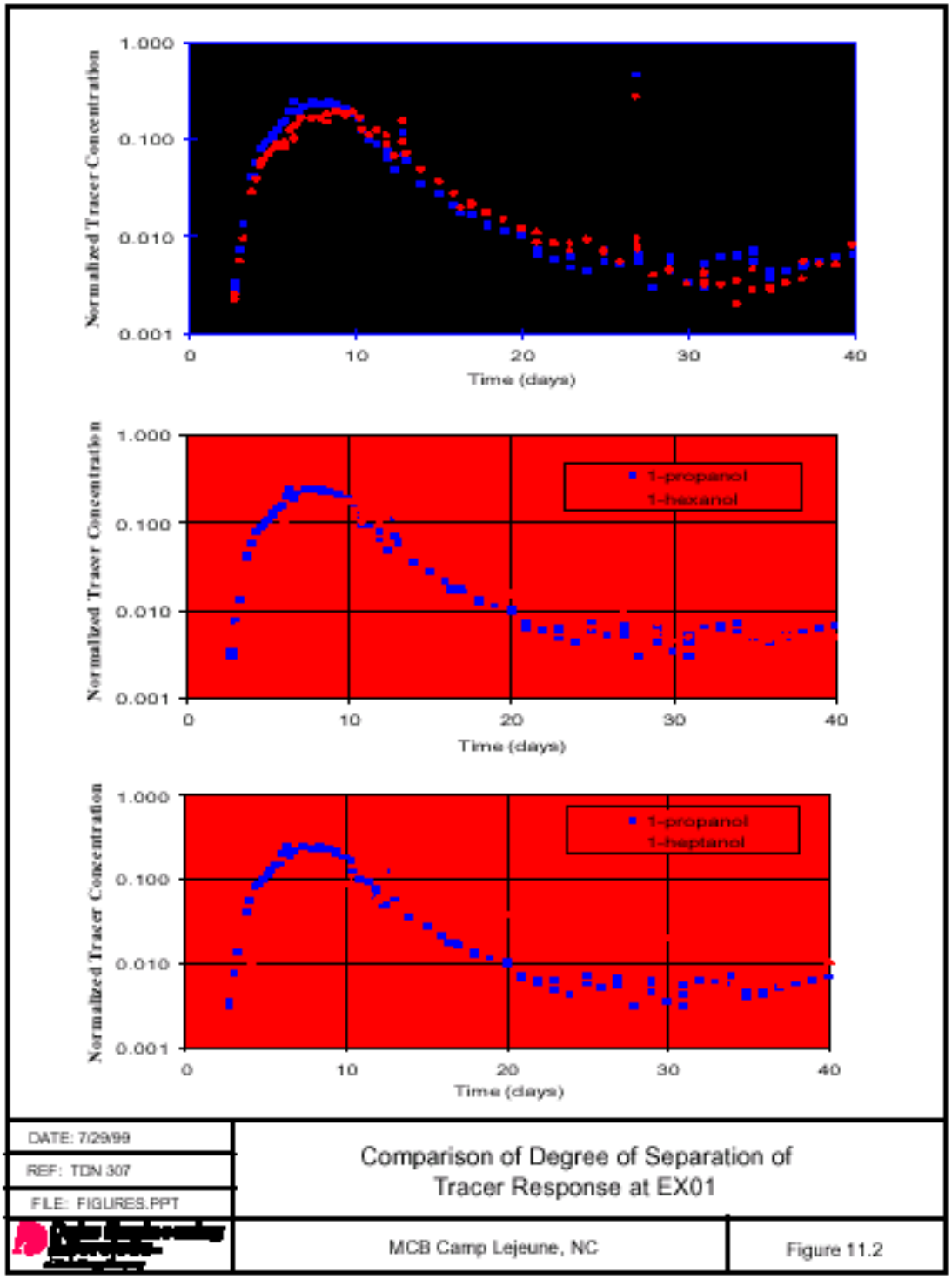

Figure 11.2. Comparison of Degree of Separation of Tracer Response at EX01

can be estimated based on the standard errors of the fitting parameters, and the DNAPL saturation estimation accuracy can be increased by increasing the accuracy of the curve fitting parameters. Figure 11.3 shows an example of the fitting parameters and the corresponding standard errors of the 1-propanol response curve for extraction well EX1.

Because the tracer concentration and the flow rate data were not recorded at the same time, a separate program was used to convert the tracer response data (which are recorded as a function of time) into a function of total volume of water extracted. The program first reads in the actual cumulative volume of fluid injected/extracted for each well as a function of time based on the information obtained from the injection/extraction logs. These data are then used as a lookup table. When the sample time/tracer concentration is read in as the input, the program interprets the corresponding volumes of water injected/extracted from the lookup table.

11.3 Method of First Temporal Moment Analysis

The theoretical foundation for the method of first temporal moment analysis of partitioning tracer tests can be found in Jin et al. (1995) and Jin (1995). This method can be used to estimate the tracer swept volume (the volume of the aquifer through which the tracer solution has flowed), the average DNAPL saturation in the tracer swept volume, and the total DNAPL volume. For a partitioning tracer test with multiple extraction wells, the following equations are applied to each individual extraction/injection well pair.

The average DNAPL saturation in the tracer swept volume (S_n) is calculated using the equation below:

$$S_n = \frac{R_f - 1}{R_f + K_p - 1} \qquad (11.1\text{-}1)$$

where K_p is the partition coefficient of the partitioning tracer, and R_f is the retardation factor defined as

$$R_f = \frac{\bar{t}_p}{\bar{t}_n} \qquad (11.1\text{-}2)$$

where $\bar{t}_p$ and $\bar{t}_n$ are the first temporal moments of the partitioning tracer and nonpartitioning tracer, respectively, and calculated using the following equations

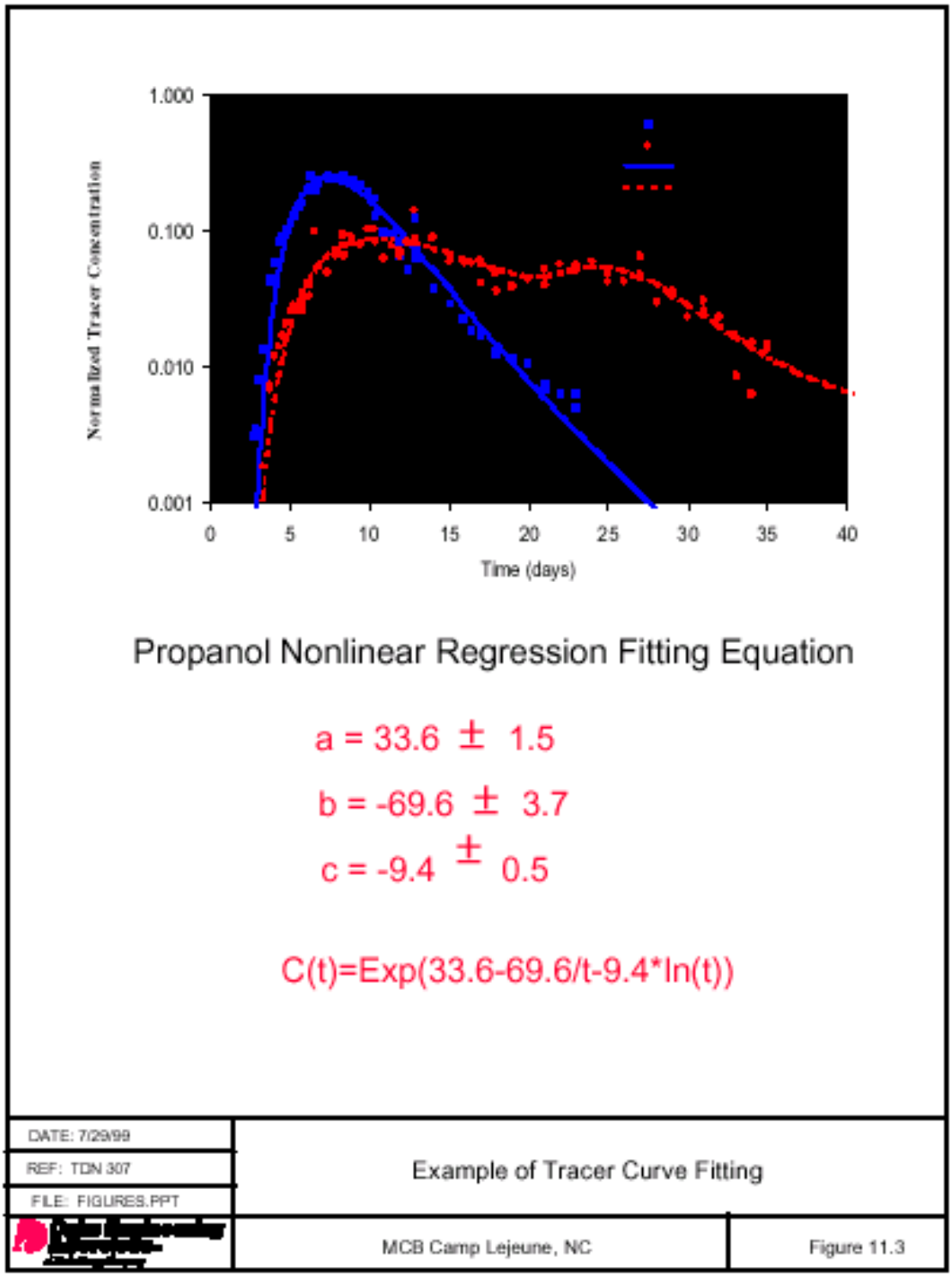

Figure 11.3. Example of Tracer Curve Fitting

$$\bar{t}_p = \frac{\int_0^{t_f} tC_p(t)dt}{\int_0^{t_f} C_p(t)dt} - \frac{t_s}{2}, \qquad (11.1\text{-}3)$$

and

$$\bar{t}_n = \frac{\int_0^{t_f} tC_n(t)dt}{\int_0^{t_f} C_n(t)dt} - \frac{t_s}{2}, \qquad (11.1\text{-}4)$$

where t_s is the slug size, i.e., the time period in which the tracer mass was injected during tracer test, t_f is the tracer test cutoff time, and $C_p(t)$ and $C_n(t)$ represent the partitioning and nonpartitioning tracer concentration as a function of time, respectively.

The average DNAPL saturation was estimated by calculating the first moments of the partitioning and nonpartitioning tracers using equations (11.1-3) and (11.1-4), by numerically integrating the corresponding tracer response curves. Next, equation (11.1-2) was used to calculate the retardation factor and then equation (11.1-1) was used to estimate the average DNAPL saturation in the swept volume.

With S_n and $\bar{t}_n$ known, the tracer swept pore volume of one particular extraction well (V_p) is now calculated as,

$$V_p = \frac{m}{M}\frac{Q\bar{t}_n}{1-S_n} \qquad (11.1\text{-}5)$$

where *M* is the total mass of tracer injected, and m is the total mass of tracer produced from the particular extraction well. Q is the total injection rate.

For the conservative tracer test, the tracer only sweeps the pore volume occupied by water. The tracer swept pore volume of the one particular extraction well in this case can be calculated as,

$$V_p = \frac{mQ\bar{t}_n}{M} \qquad (11.1\text{-}6)$$

11.4 PITT Data Analysis

11.4.1 Extraction Well Tracer Data Analysis

Tracer concentrations for PITT samples were normalized to tracer injectate concentrations. Normalized concentrations, which are dimensionless, are calculated by dividing each measured sample concentration by the averaged tracer injectate concentration (also measured by GC analysis). The normalized tracer concentration histories and the corresponding fitted curves for the six extraction wells are shown in Figures 11.4a through 11.9. In each of the figures presented, the top graph shows the tracer concentration in a linear scale and the bottom in a semi-log scale. The linear scale graphs show the separation of tracer peak concentrations better while the semi-log scales give more information on the tailing of tracer response curves.

The data for only one conservative tracer (1-propanol) and two partitioning tracers (1-hexanol and 1-heptanol) data are presented in these figures. This is because the partition coefficient of 4M2P is very small, and negligible chromatographic separation was observed in this PITT between 4M2P and the conservative tracer. The separation of the tracer response between 1-propanol and 1-heptanol in all six extraction wells clearly indicates the presence of DNAPL in the pore space swept by the partitioning tracers. Since the degree of separation is different for each well, it can be inferred that the DNAPL is not uniformly distributed in the pore space swept by the partitioning tracers. Since the degree of tracer separation decreases for the wells farther away from the building, this also implies that most of the DNAPL in the test zone is near the building.

The tracer curves were analyzed using the method of first temporal moment as presented in Section 11.1 of this report. The resulting estimates of the DNAPL volume within each interwell swept pore volume are summarized in Table 11.1. The pore volume (shown as swept volume) of the aquifer swept by the tracers, for each interwell pair, as determined by the moment analyses is also shown in this table. The total aquifer pore volume swept by the tracers was 4,780 gallons as determined by summing the swept volumes calculated for each interwell pair. Moment analysis of the tracer response curves gives an estimated volume of 87 gallons of DNAPL in this swept pore volume, corresponding to an average DNAPL saturation of 1.8% throughout the test zone. The cumulative tracer recovery for 1-propanol is 85%. The cumulative tracer recovery for 1-propanol is 85%. The recoveries of the other tracers used are approximately the same, in the range of 85% $\pm$ 3%.

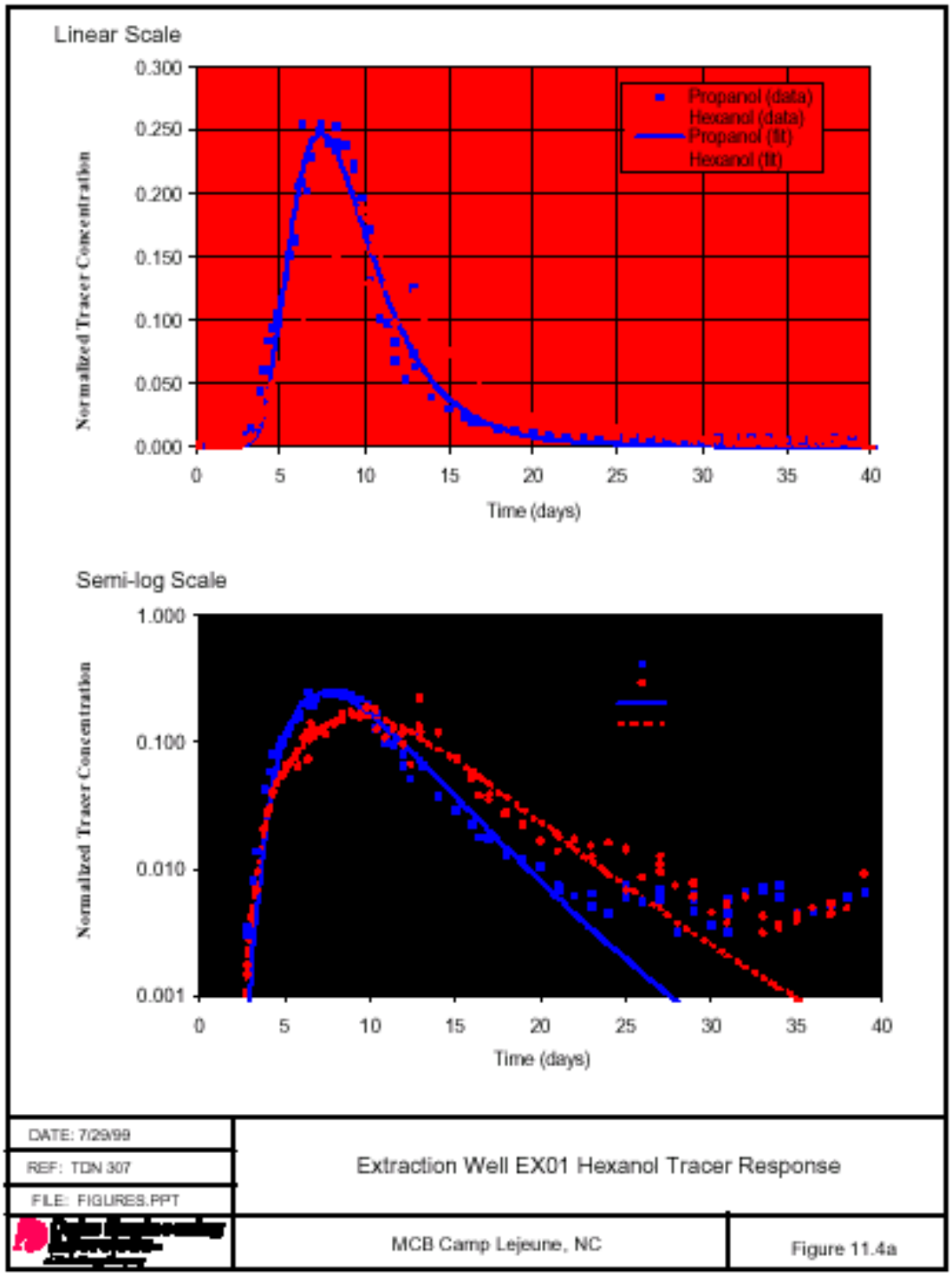

Figure 11.4a. Extraction Well EX01: Hexanol Tracer Response

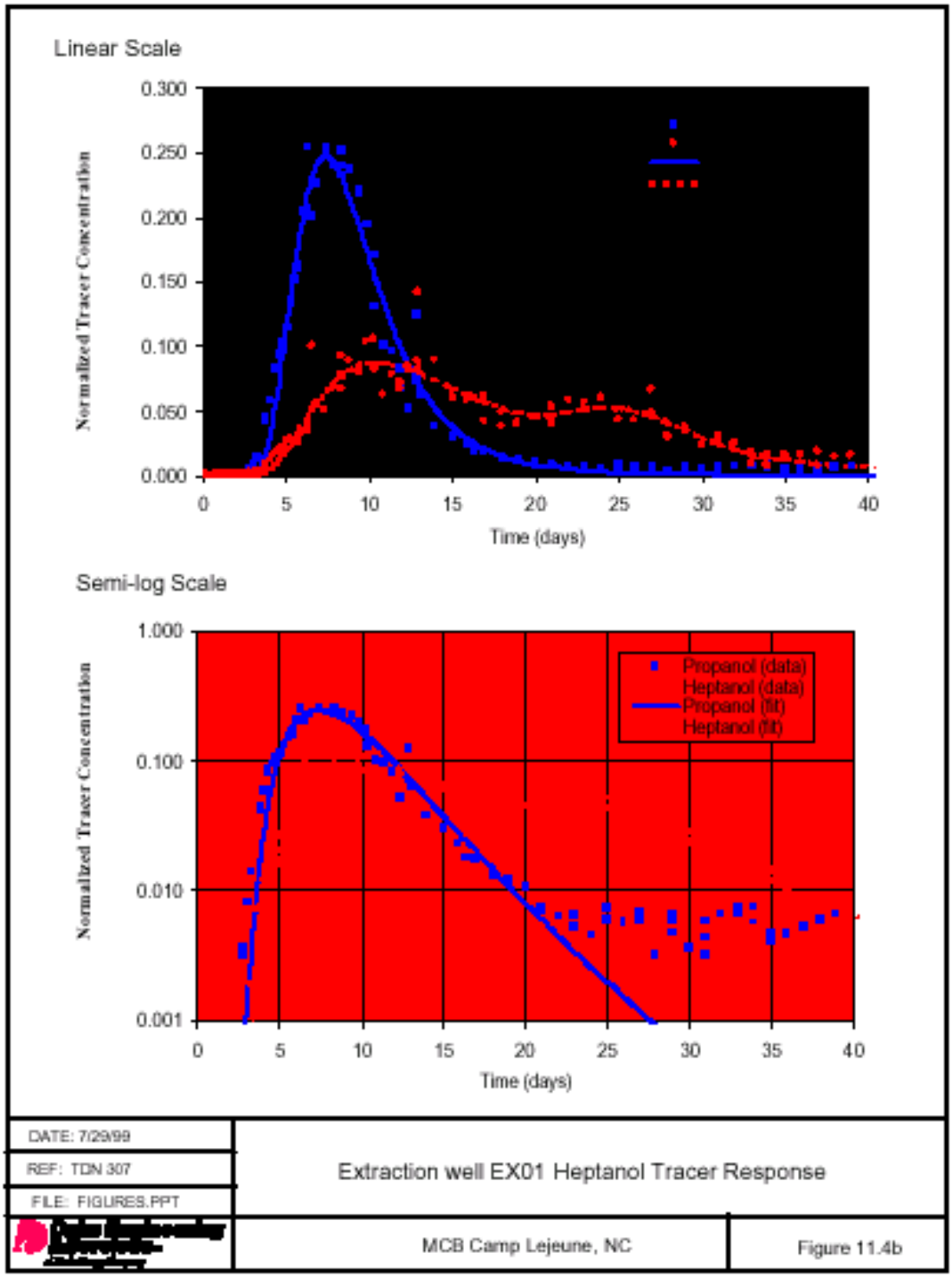

Figure 11.4b Extraction Well EX01: Heptanol Tracer Response

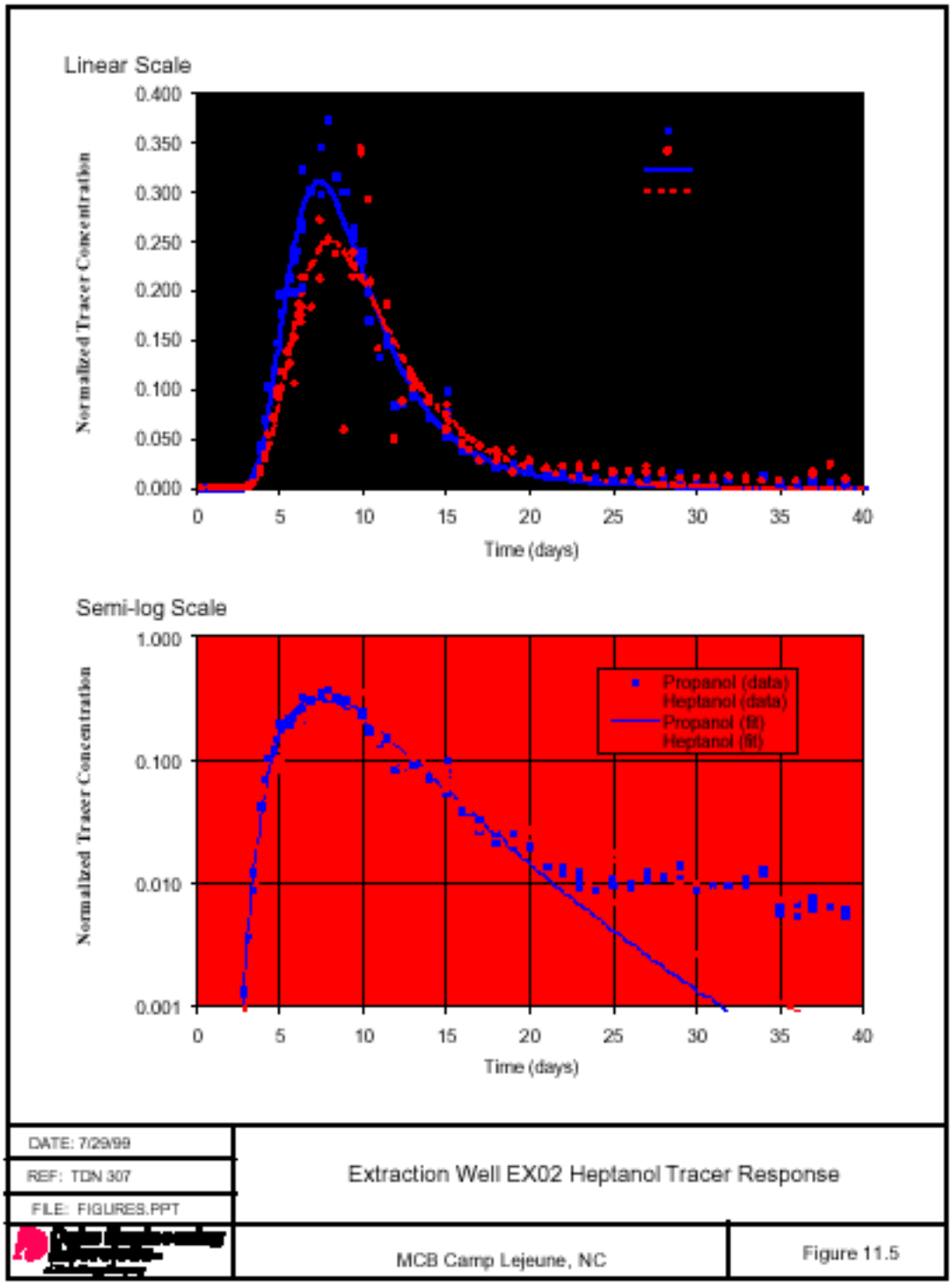

Figure 11.5 Extraction Well EX02: Heptanol Tracer Response

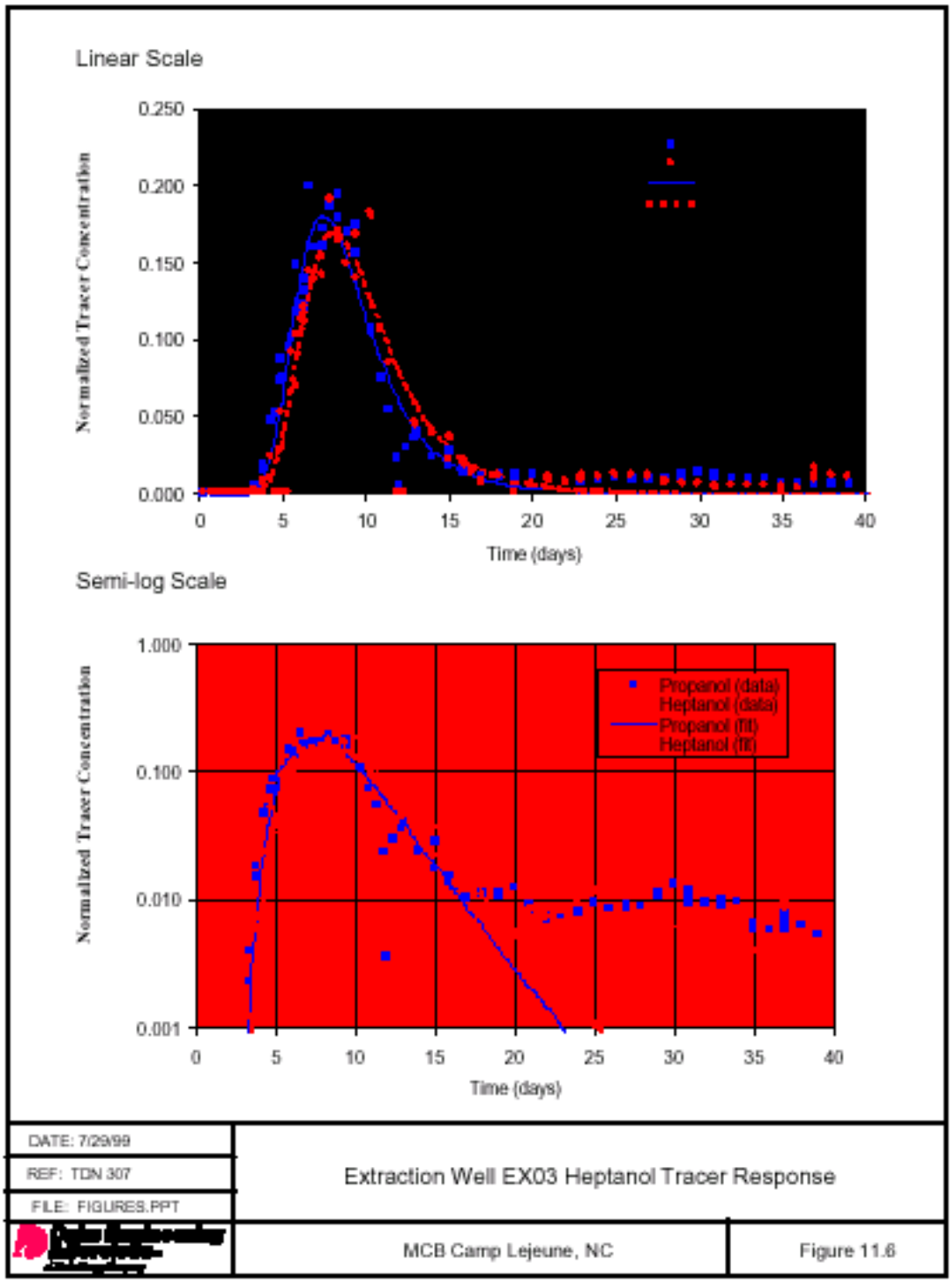

Figure 11.6 Extraction Well EX03: Heptanol Tracer Response

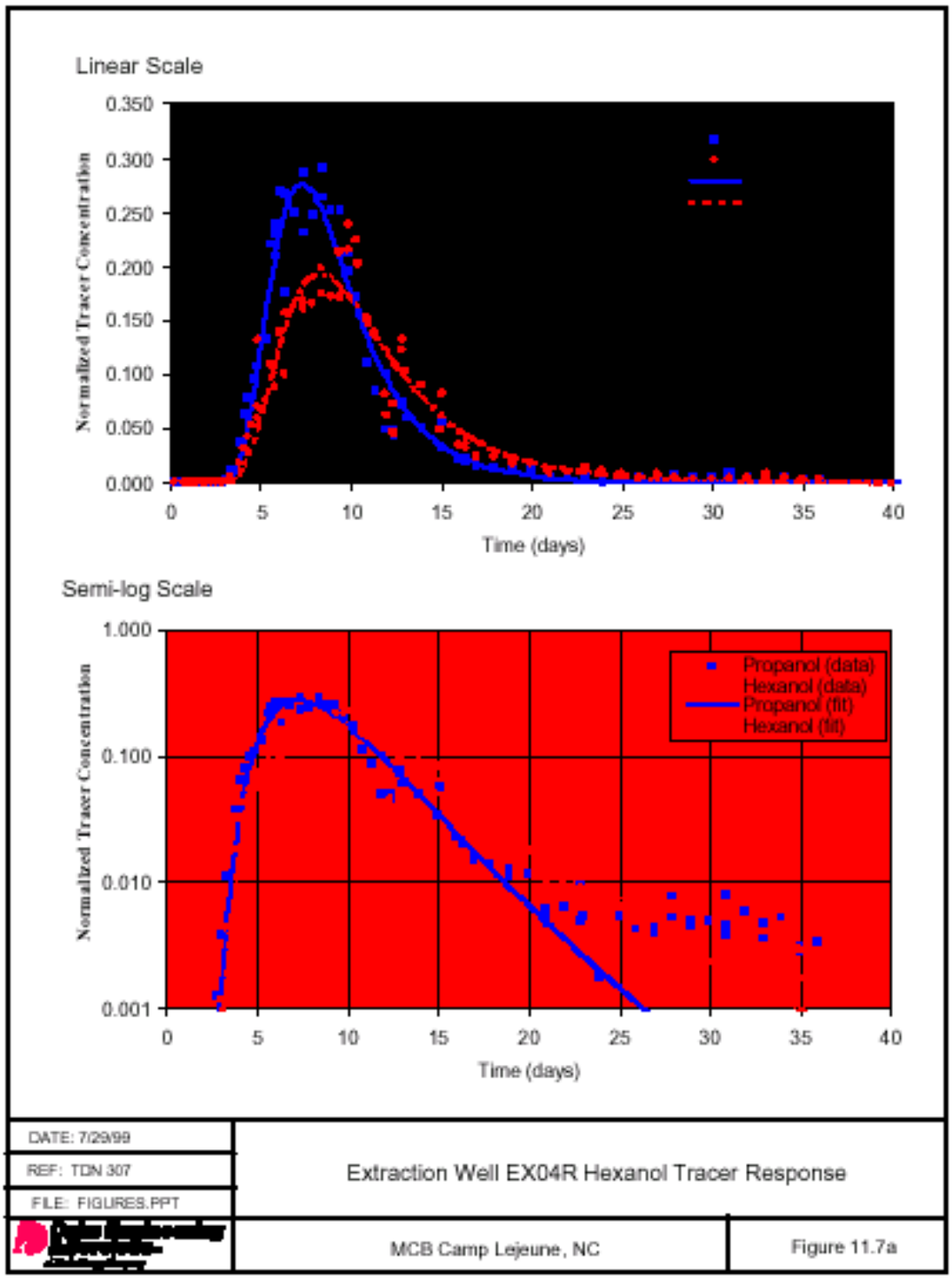

Figure 11.7a Extraction Well EX04R: Hexanol Tracer Response

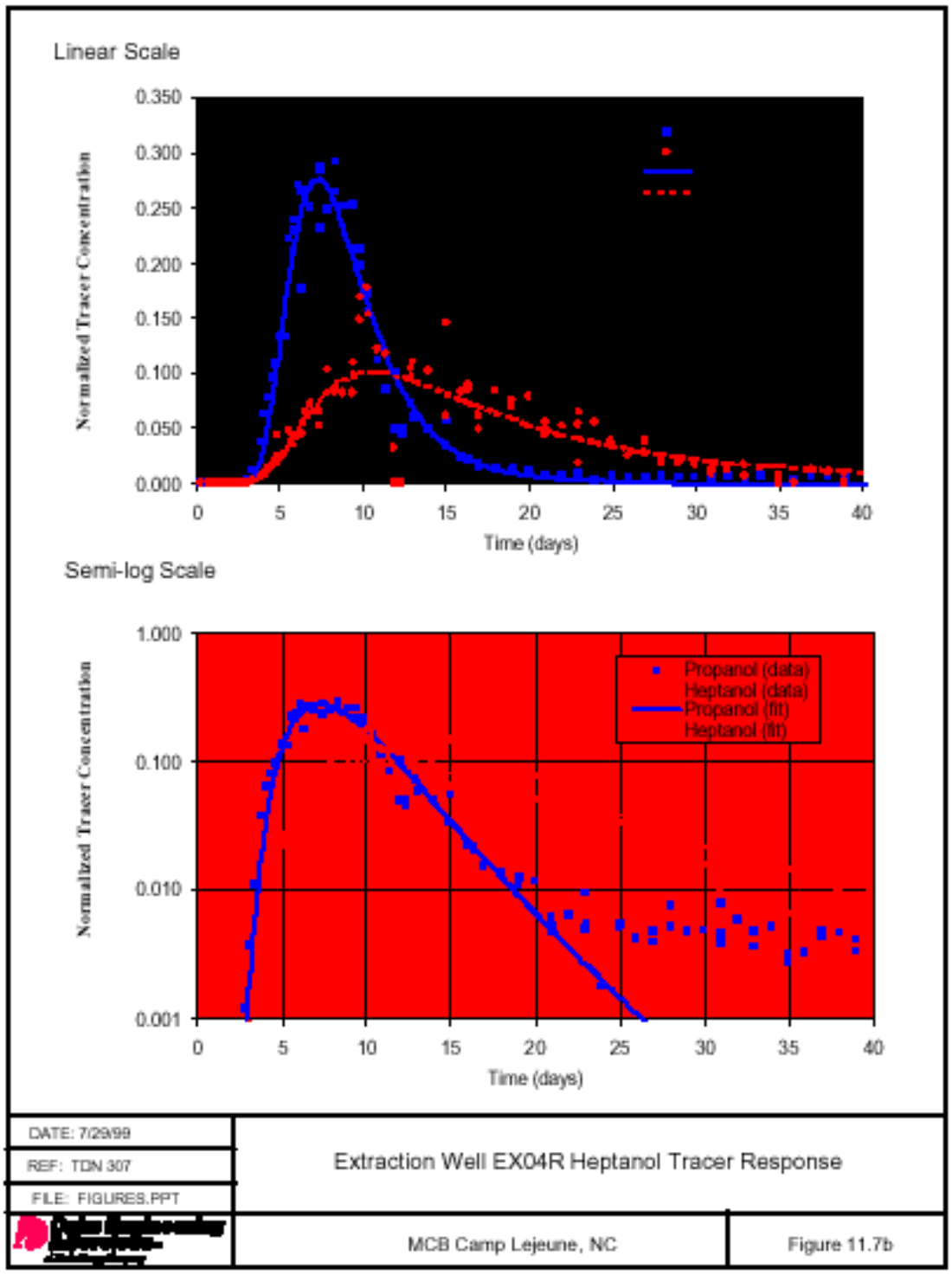

Figure 11.7b Extraction Well EX04R: Heptanol Tracer Response

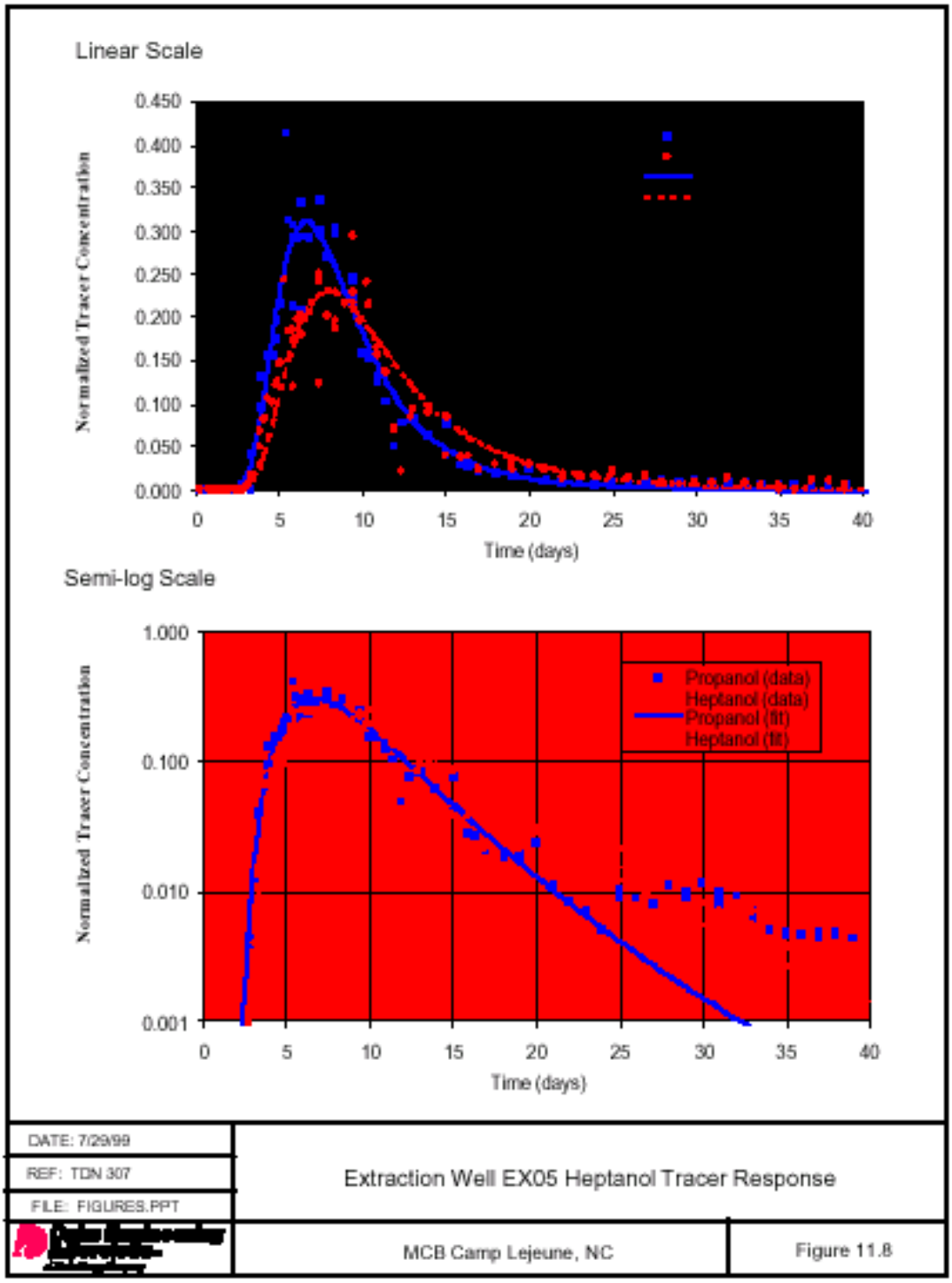

Figure 11.8. Extraction Well EX05: Heptanol Tracer Response

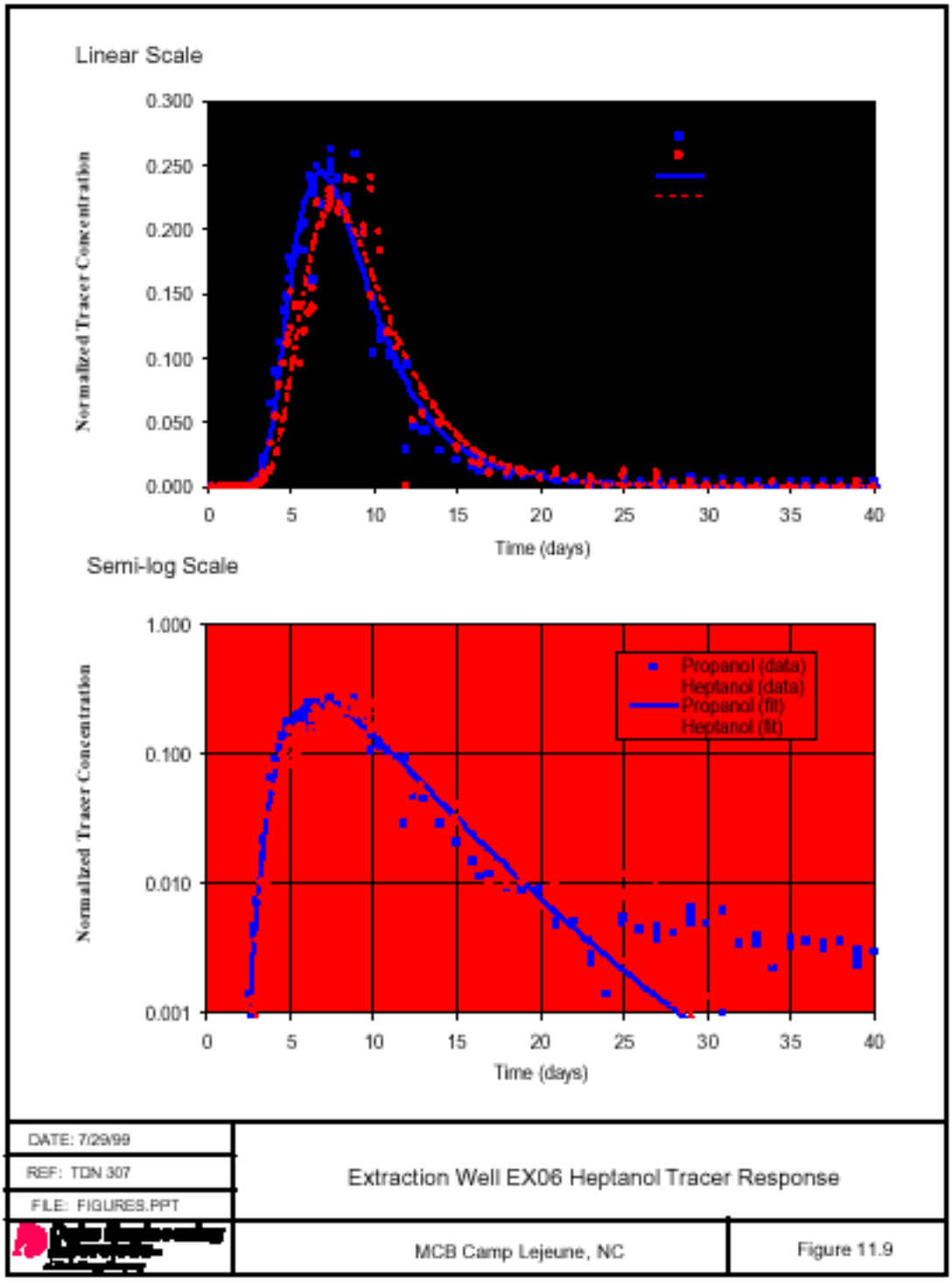

Figure 11.9. Extraction Well EX06: Heptanol Tracer Response

Table 11.1 Summary of Extraction Well PITT results

Well	Recovery (%)	Swept Volume (gals)		Saturation (%)		PCE Volume (gals)	
		1-Hexanol	*1-Heptanol*	*1-Hexanol*	*1-Heptanol*	*1-Hexanol*	*1-Heptanol*
EX01	13	790	790	4.1	3.9	33	31
EX02	17		1030		0.5		5
EX03	10		540		0.4		2
EX04R	14	790	790	3.7	4.5	29	36
EX05	17		890		1.0		10
EX06	14		740		0.4		3
Total	85		4780		1.8		87

11.4.2 Multilevel Sampler Tracer Data Analysis

Tracer concentration histories for three multilevel sampling points MLS 2-17, MLS 3-17.5, and MLS 2-18.5 (ft bgs) are shown in Figure 11.10. Tracer data from the six other multilevel sampling points was not available because these sampling points were incapable of yielding a sufficient flow to collect a viable sample, as discussed in Section 10.2.

The chromatographic separation of the partitioning tracer response at the three viable MLS sampling points confirms the existence of DNAPL at these depth locations. Based on the observation and analysis of the partitioning tracer data, several conclusions were drawn. First, the degree of tracer separation in monitor points MLS 2-17, MLS 3-17.5, and MLS 2-18.5 is observed to increase with depth, as shown in Figure 11.10. Based on this observation, it is concluded that DNAPL saturation tends to increase with depth near the base of the shallow aquifer, which implies that the majority of the DNAPL is localized in the silty layer immediately above the clay aquitard. This coincides with soil sampling observations during the initial DNAPL zone investigations. Second, the MLS data shows the non-partitioning tracer breakthrough and peak times are significantly later in the basal silt layer compared to the overlying fine sands. From this it can be inferred that the hydraulic conductivity of the silty layer at the base of the shallow aquifer is lower by a factor of approximately 4 when compared to the overlying fine sands. This has important implications for the SEAR design, as discussed in Section 12.

The MLS tracer data was analyzed by the same method as used for the extraction well tracer data, except that the MLS data analysis was limited to calculating DNAPL saturation but not DNAPL volume. This is because the MLS sampling points are monitor points along the tracer flow path between the injection and extraction wells, and

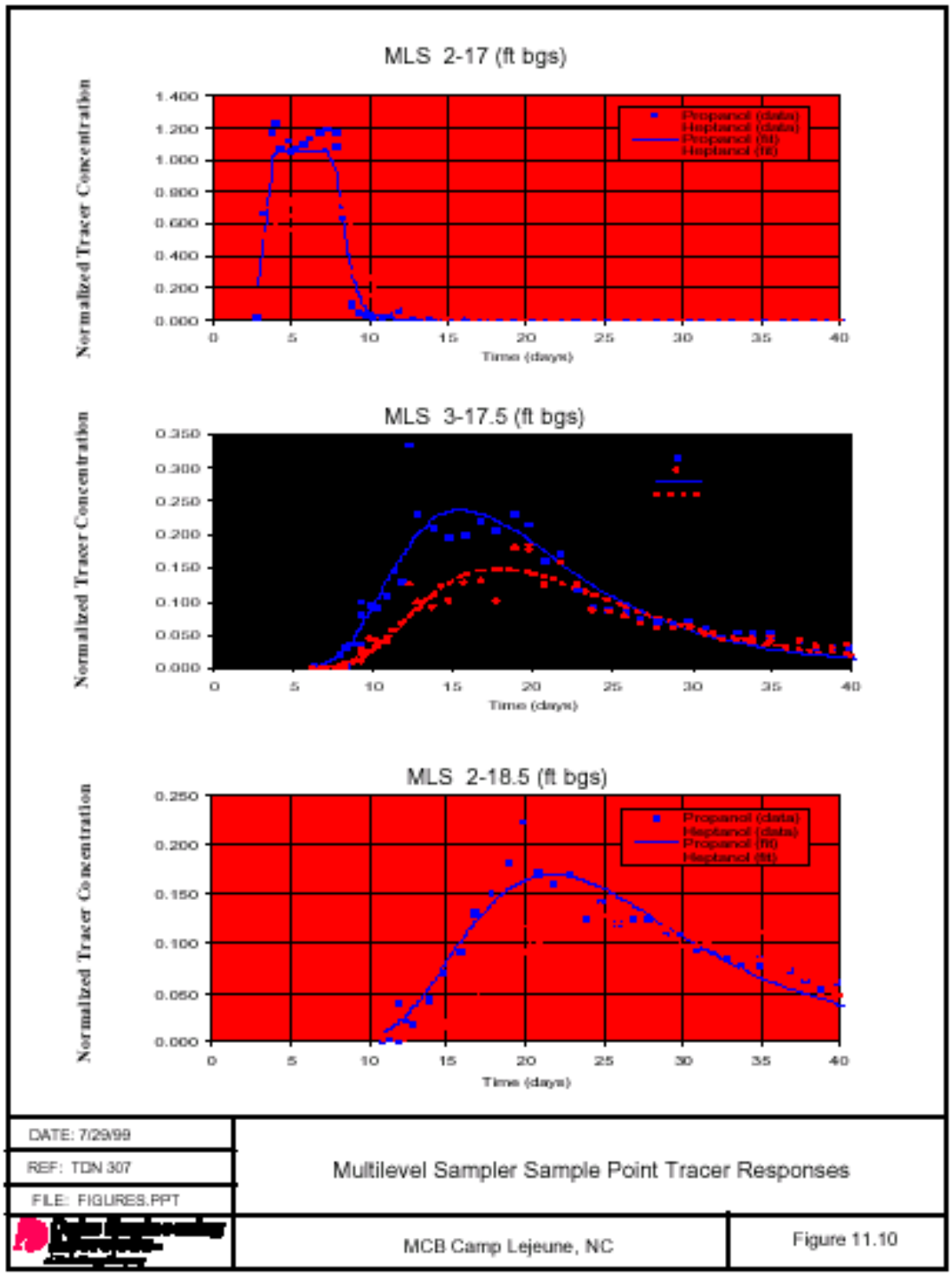

Figure 11.10. Multi-Level Sample Point Tracer Responses

there is no flow rate associated with the MLS sample points. The flow rate (Q) at an extraction well is required to calculate the swept pore volume, as shown in equation 11.1.5, which is then used to calculate DNAPL volume in the swept pore volume between a given pair of injection and extraction wells. It should also be noted that the estimated value of DNAPL saturation at each MLS point does not represent the DNAPL saturation at the monitor point, but rather, it is the average DNAPL saturation in the steamtube (tracer flowpath) from the injection well to the MLS monitor point. Based on moment analysis of MLS tracer data for MLS-2 and MLS-3, it is estimated that the average DNAPL saturation is approximately 0.5% in the higher permeability layer (overlying fine sand), and about 3.6% in the lower permeability (basal silt) layer. It is likely that the DNAPL saturations are higher than this at locations closer to the building, however MLS-1 (located between IN01 and EX01; see Figure 4.1) was not functional for sampling, therefore there is no tracer data at this near-building MLS location.

The effective permeability contrast at the different MLS depths is represented by the ratio of the first moments for the non-partitioning tracer response curves at the different MLS monitor points. The results indicate that the effective permeability of the basal silt layer is about four times lower than that of the overlying fine sands, and permeability may be even lower near the basal contact of the shallow aquifer at the aquitard. However, no PITT samples were successfully collected from the lowest MLS sampling points, i.e., just above the aquitard, to confirm this possibility.

A summary of the DNAPL saturation estimates based on the MLS tracer data is summarized in Table 11.2. The results for effective permeability contrast estimation are shown in Table 11.3.

Table 11.2 Summary of Multilevel Sampler (MLS) Tracer Data Analysis Results

MLS	Saturation (%)
2-17.0	0.7*
3-17.5	0.5
2-18.5	3.6

* High uncertainty due to the quality of the data.

Table 11.3 Estimated Effective Permeability Contrast

MLS Pair	k Ratio
2-17.0 / 3-17.5	2
2-17.0 / 2-18.5	4
3-17.5 / 2-18.5	2

11.4.3 Comparison of PITT results to Simulation Predictions

The PITT data for the non-partitioning tracer, 1-propanol, is plotted against the UTCHEM simulation predictions for a non-partitioning tracer in Figures 11.11 to 11.13. These figures show excellent agreement between predicted and actual tracer response. However, tracer recoveries obtained during the PITT (85% ± 3%) were lower than the original simulation prediction of 93% to 96%. As mentioned earlier, the water level and pumping rate data recorded continuously during the PITT show that hydraulic control was maintained throughout the PITT. A water level contour map produced using this data, provided as Figure 11.14, further supports this conclusion. As such, the lower than expected tracer recovery should not be due to loss of tracer out of the demonstration area. The most likely explanation for the lower tracer recovery is that the analyzed/reported tracer concentrations are lower than actual sample concentrations. The laboratory that analyzed the PITT samples experienced analytical problems as discussed in Sections 10.3 and 11.1, which may have contributed a low-level systematic underestimation of tracer concentrations for the PITT samples.

In addition to analytical difficulties, biodegradation of the tracers in the subsurface may have contributed to tracer loss to a minor degree. Biodegradation of the tracers may have been favored by the relatively high ground water temperature (due to the adjacent steam vault) and noted organic content of the aquifer. While the impact of analytical errors and biodegradation is not easily quantified, they provide reasonable explanations for the deviation of actual tracer recoveries from the originally estimated value. Lessons learned from the GC analysis of PITT samples from this initial PITT at Site 88 will be used to fine-tune the GC method for more accurate and reliable operations for the final (post-SEAR) PITT.

11.5 Error Analysis

There are two main sources of errors associated with the analysis of partitioning tracer data, which may contribute to uncertainty in the estimates of average DNAPL saturation. The first source of error, ΔR_f, is an uncertainty in the estimation of the retardation factor based on the actual tracer data for a pair of tracers (i.e., as a function of scatter in the non-partitioning and partitioning tracer datasets). The second source of error, ΔK, is due to the uncertainty in the partition coefficient measurement. Based on the theory of error propagation (Taylor, 1997; pg. 79), the error for DNAPL saturation, ΔS_N, which accounts for the cumulative error from ΔR_f and ΔK, can be derived from equation 11.1-1, as:

$$\Delta S_N = \sqrt{\left(\frac{K}{(R_f + K - 1)^2}\Delta R_f\right)^2 + \left(\frac{R_f - 1}{(R_f + K - 1)^2}\Delta K\right)^2} \qquad (11.5\text{-}1)$$

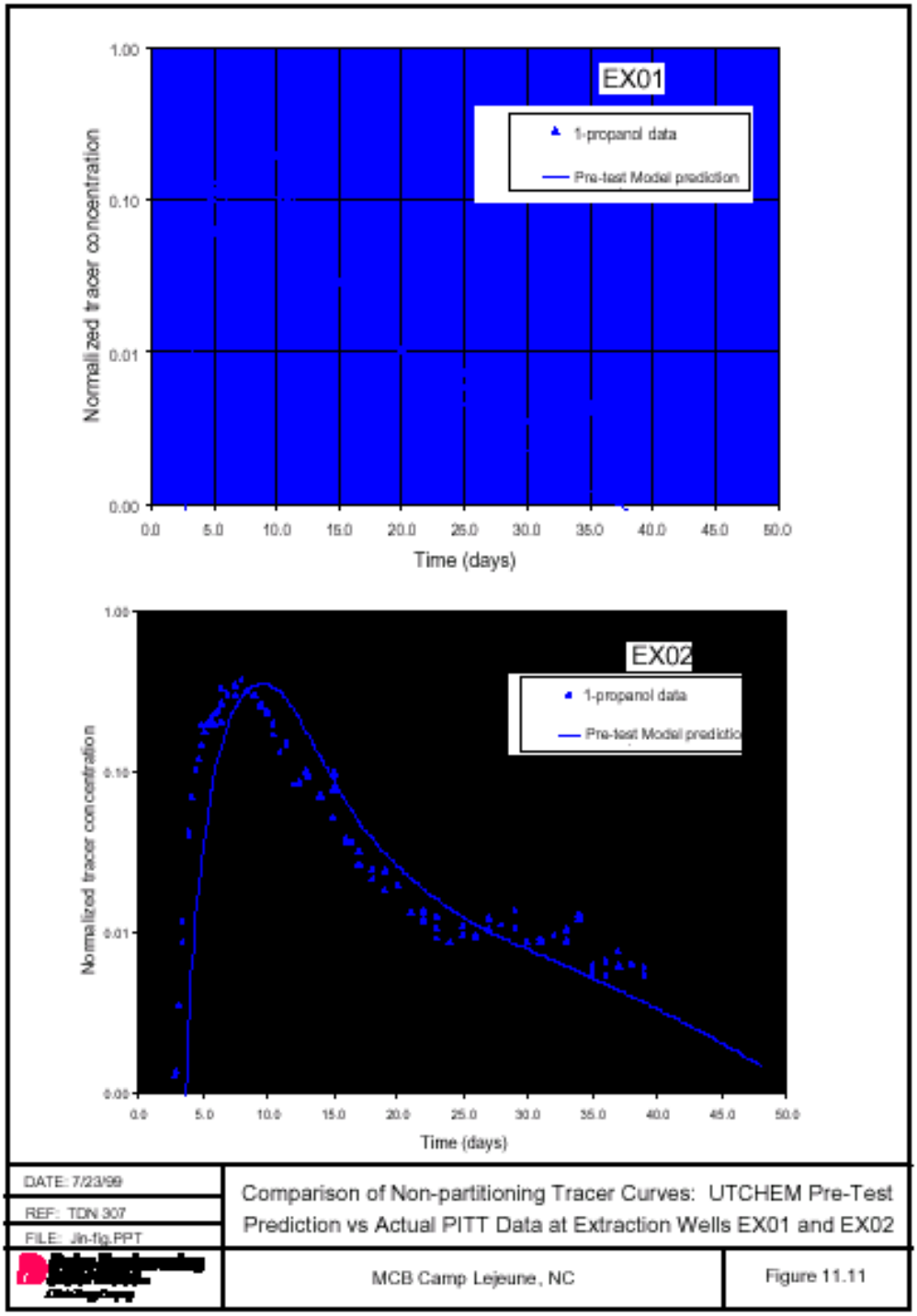

Figure 11.11. Comparison of Non-partitioning Tracer Curves: UTCHEM Prediction vs. Actual PITT Data at Extraction Wells EX01 and EX02

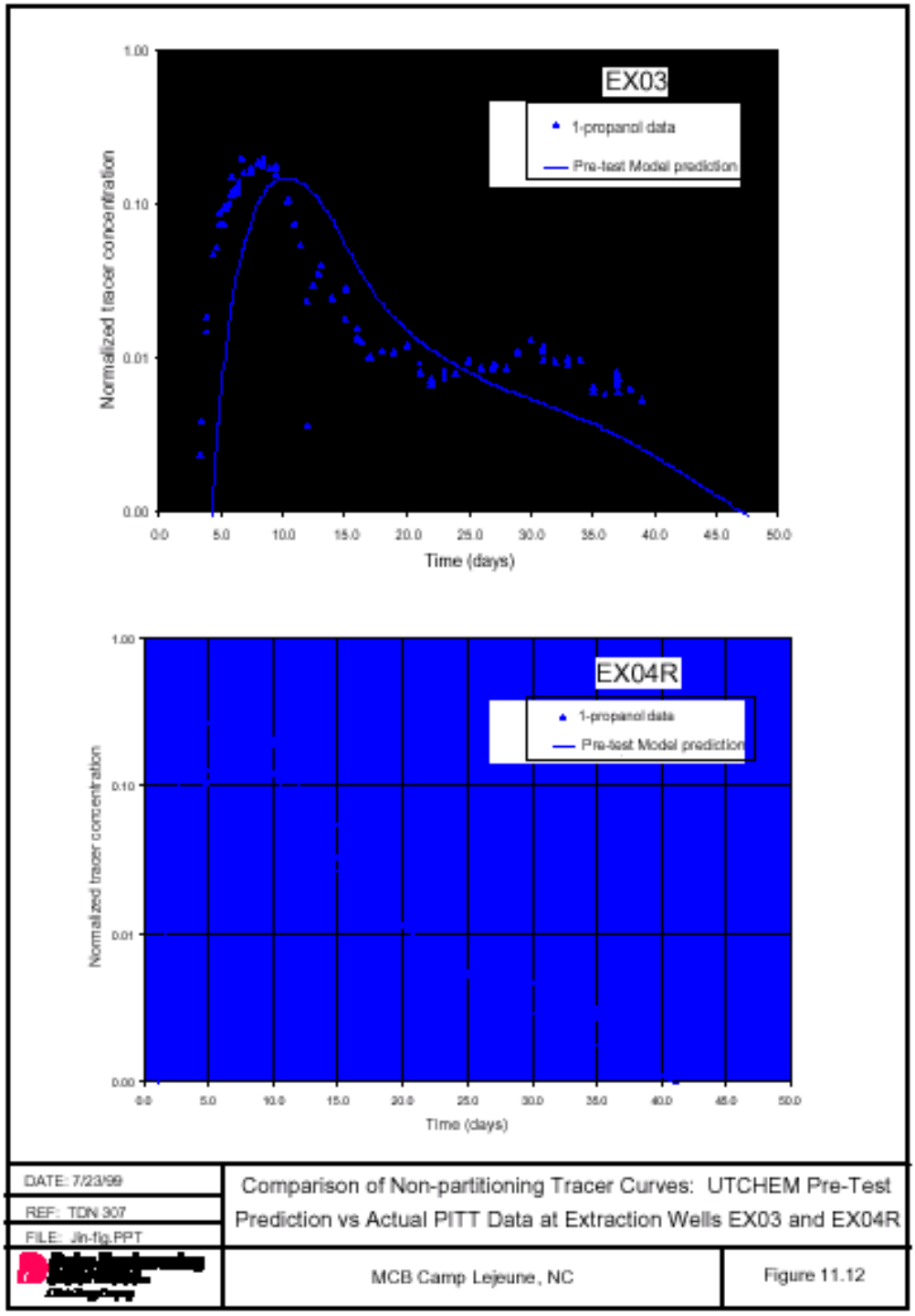

Figure 11.12. Comparison of Non-partitioning Tracer Curves: UTCHEM Prediction vs. Actual PITT Data at Extraction Wells EX03 and EX04R

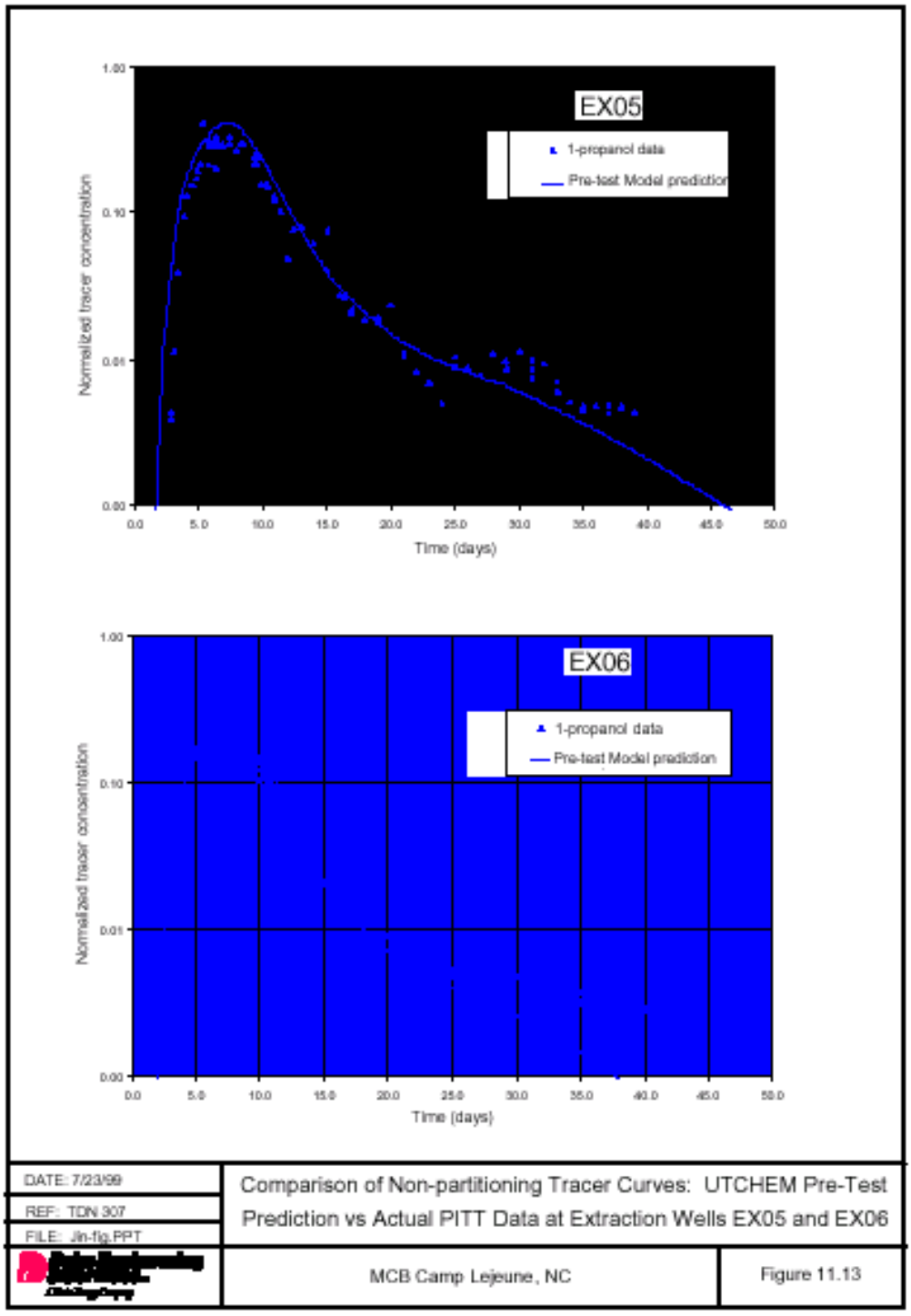

Figure 11.13. Comparison of Non-partitioning Tracer Curves: UTCHEM Prediction vs. Actual PITT Data at Extraction Wells EX05 and EX06

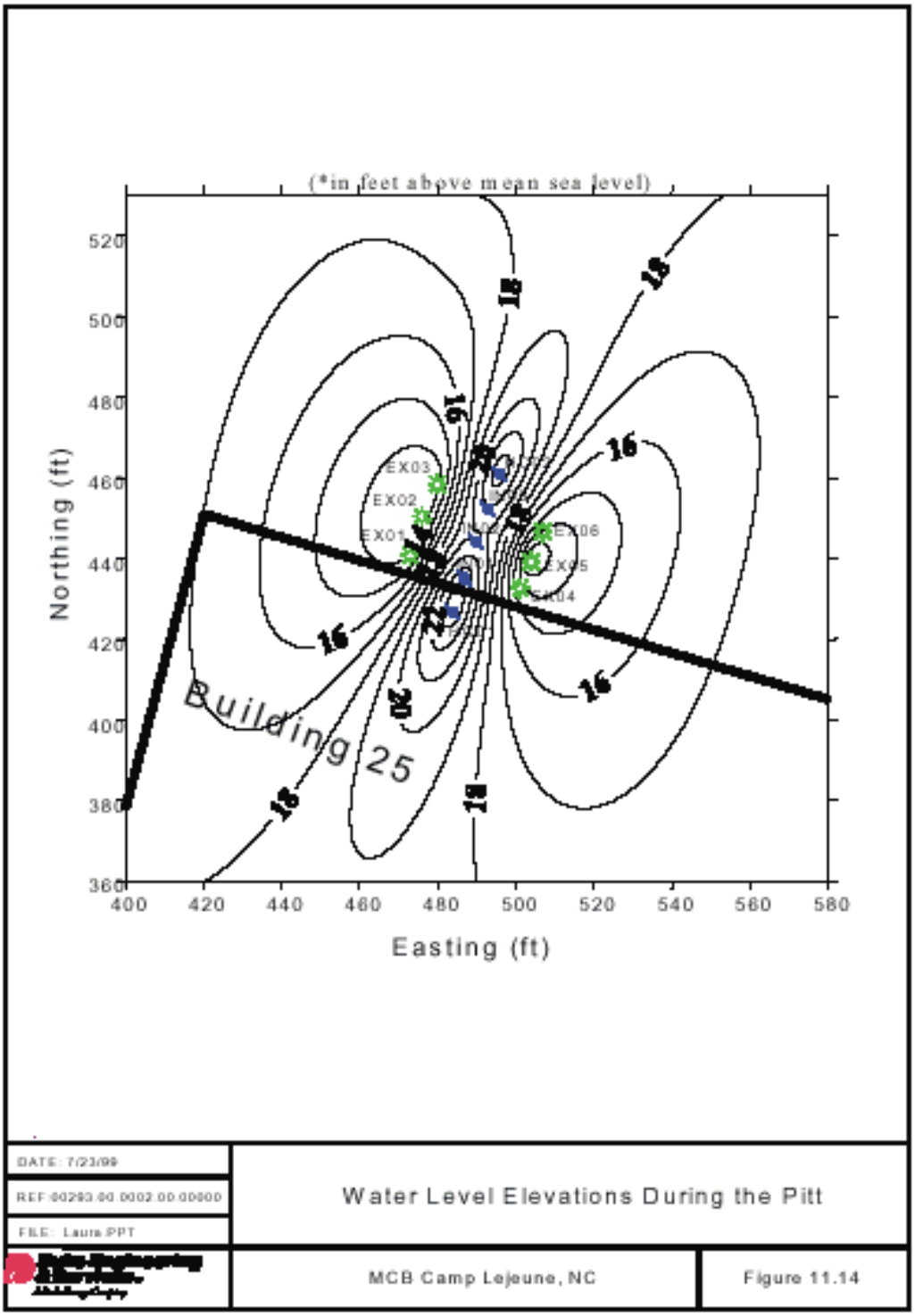

Figure 11.14 Water Level Elevations During the PITT

The first source of error, ΔR_f, can be estimated based on the standard error of the fitting parameters, as discussed in Section 11.2 of this report. A detailed discussion on estimating the standard error of the retardation factor from standard errors of the fitting parameters can be found in a recent paper by Jin and Pope (1998). Table 11.4 summarizes the retardation factor estimated error of the retardation factor ($R_f \pm \Delta R_f$) and the percent error of the retardation factor ($\Delta R_f/R_f$) for 1-heptanol at each extraction well.

The second source of error can be estimated based on error analyses of numerous laboratory measurements of the tracer partition coefficient. It was found that the average relative error in the partition coefficient measurement, ΔK, is expected to be about 10% (G.A. Pope, University of Texas at Austin, personal communication, 1998). The laboratory measured partition coefficient of 1-heptanol is 35. This means that the uncertainty of the partition coefficient of 1-heptanol is 35 ± 3.5, which is a conservative estimate for ΔK given the % uncertainty in the lab measurements of K reported in Table 7.1.

Based upon these two sources of error, the uncertainty of saturation estimates using equation 11.5-1 is summarized in Table 11.5.

Table 11.4 Uncertainty of DNAPL Saturation Estimates (1-propanol vs. 1-heptanol)

Well	$R_f \pm \Delta R_f$	$\Delta R_f/R_f$ (%)	$S_N \pm \Delta S_N$	$\Delta S_N/S_N$ (%)
EX01	2.45 ± 0.08	3.30	3.90 ± 0.44	11.2
EX02	1.16 ± 0.01	0.34	0.45 ± 0.05	11.5
EX03	1.13 ± 0.01	0.48	0.36 ± 0.04	10.7
EX04R	2.65 ± 0.37	14.0	4.50 ± 1.06	23.5
EX05	1.38 ± 0.02	1.10	1.07 ± 0.11	10.7
EX06	1.12 ± 0.01	0.88	0.35 ± 0.05	12.9

Note: $K \pm \Delta K = 35 \pm 3.5$ for 1-heptanol; and $\Delta K/K$ (%) = 10

As Table 11.4 indicates, the relative error of the retardation factor ($\Delta R_f/R_f$) is generally small (<~3%) compared to the relative error of the tracer partition coefficient estimation, i.e., 10%. The only exception in this case is EX04R where the relative error of the retardation factor is somewhat higher due to the scattering of the GC tracer data.

In general, the uncertainty of DNAPL saturation estimation is inversely proportional to the tracer partition coefficient as shown in equation 11.5-1. Tracers with higher partition coefficients will lead to larger retardation factors and improved accuracy in DNAPL

volume estimation. This has also been illustrated on a theoretical basis by Jin (1995). In practice, the retardation factor has to be at least 1.2 in order to have a reliable DNAPL volume and saturation estimate. If the tracers with large partition coefficients, such as 1-heptanol, still yield retardation factors in the range of 1.0 to 1.1, it means that there is little, if any, DNAPL present in the subsurface being tested.

The above analysis of potential DNAPL saturation estimation error does not account for errors which may be due to uneven distribution of Varsol™ across the site (i.e., Varsol that is dissolved in the PCE DNAPL). Recently collected (free-phase) DNAPL samples indicate that at extraction wells EX01 and EX04, Varsol™ concentrations may be as high as 4-14 wt% of the DNAPL. Previously, Varsol™ concentrations had not been observed to exceed 2 wt%. Based on the Equivalent Alkane Carbon Number (EACN) approach (Dwarakanath and Pope, 1998), it is possible to estimate the influence of Varsol™ on the estimated DNAPL saturation. Using this approach, with 4-14 wt% Varsol™ present in the DNAPL, the underestimate in DNAPL saturations by PITT data analysis would be between 2-5% (see Appendix Q), which is relatively negligible.

A final source of estimation error is from the extrapolation of experimental data. Extrapolation of experimental data is required when the tails of the tracer concentration histories are not fully characterized due to limitations in the GC detection limits. This can cause under prediction of the average DNAPL saturation and hence cause estimation errors. These errors would be large or small depending on the quality of the tracer data. The data extrapolation technique is very simple and sound in its principle. However if there is significant scattering in the tracer concentration tail due to the effect of analysis errors and low tracer concentrations (on the order of the detection limit), a great deal of engineering judgment and subjectivity may be required to pick the correct exponential decline of the tracer tail. The average DNAPL saturations are highly sensitive to the changes in the slope of the exponential decline curve and this can cause a relatively large uncertainty in the average DNAPL saturation estimates. On the other hand, if the tracer data is of good quality and a linear decline in tracer concentrations on a semi-log plot is observed, the extrapolation errors will be minimal. If extrapolation errors are minimal, the result will be a significant increase in the overall estimation accuracy of the average DNAPL saturations. The tracer data shows reasonably linear declines in tracer concentrations on the semi-log plots for data above the detection limit (Figures 11.4a to11.9), and it is our professional judgement that any error associated with extrapolation of the data is not significant with respect to the resulting estimates for DNAPL saturation.

The above error discussion is based on the assumption that all observed tracer retardation is due to tracer partitioning to DNAPL. However, the column test experiments, discussed in Section 7, have shown that the elevated sedimentary organic content, as a result of peat particles in the sediments, can lead to tracer sorption to the natural organic matter which gives an apparent response for the presence of DNAPL in uncontaminated sediments. Pre-PITT soil sampling indicated that little or no DNAPL is

likely present in the zone between EX03 and EX06 (see Figure 3.3). The tracer response at EX03 and EX06, which lead to a combined estimate of approximately 5 gallons of DNAPL for these two interwell locations, may actually be due to tracer interference with the sedimentary organic carbon, i.e., peat, in the sediments. Furthermore, it is likely that of the DNAPL measured by the PITT at EX02 and EX05 (0.5% and 1.0% saturations, respectively), a significant portion of the tracer retardation was due to tracer sorption to the peat. It is not, however, believed that the peat played any significant role in the tracer response at wells EX01 and EX04R, where DNAPL saturations were measured to be 3.9 and 4.5%, respectively.

11.6 Summary and Conclusions of PITT Results

Moment analysis of the PITT data estimated a DNAPL volume of 87 gallons in the swept volume of about 4,800 gallons. The DNAPL is non-uniformly distributed in the geosystem and the majority of the DNAPL is localized in the basal silt layer overlying the aquitard. There is a tendency for the DNAPL saturation to increase with depth and decrease laterally away from the building. The measured average DNAPL saturation for the well pairs near the building is about 4.5%, and 0.4% for the well pairs away from the building.

However, it should be noted that although the results from the PITT are reliable, the DNAPL volume estimation of 87 gallons is not exact. There are several factors that could contribute to an overestimate or underestimate of DNAPL in the test zone. The presence of peat particles in DNAPL-zone sediments, which elevates the sedimentary organic carbon content in the sediments, has been shown in column tests to interfere with tracer retardation such that DNAPL appears to be present in uncontaminated sediments at low-level DNAPL saturations of approximately 0.3% to 0.5%. Unless this is accounted for, it may lead to overestimation of the volume of DNAPL in the test zone. It is believed that this interference is responsible for an apparent volume of approximately 13 gallons of DNAPL in the swept pore zones represented by samples collected from extraction wells EX02, EX03, EX05, and EX06. Therefore, the corrected estimate for the total volume of DNAPL measured by the PITT is 74 gallons. This correction is based upon the results of soil column tests which showed an apparent DNAPL saturation of 0.3 to 0.5% in uncontaminated soil. It is possible that the actual volume of DNAPL is even somewhat lower than 74 gallons since the degree of tracer sorption to natural organic matter is a function of the degree of the f_{oc} present in uncontaminated and/or in low-level DNAPL-contaminated portions of the test zone. The column experiments were conducted with fine sand sediments with f_{oc} values that ranged from 1200 to 2100 mg/kg (Section 7.4.1). However, f_{oc} analyses conducted on three soil samples collected from the basal, fining downward sediments in the DNAPL zone (grading from fine sand to clayey silt just above the aquitard contact) resulted in f_{oc} values that range from 1500 to 6400 mg/kg (Table 3.2).

Conversely, factors that may have contributed to an underestimate of DNAPL include: (1) the presence and production of free-phase DNAPL during the PITT; (2) slightly lower tracer recovery by chemical analysis after the holding time had expired; and (3) the higher than anticipated Varsol concentrations in the DNAPL. These factors have not been quantified in the error analysis, as presented in the above section. Taking these factors into account, it is estimated that an additional 14 gallons of DNAPL may be present in the test zone for a total of about 88 gallons.

12.0 SUMMARY AND CONCLUSIONS

Duke Engineering & Services completed characterization of a PCE DNAPL zone at Site 88, US Marine Corps Base, Camp Lejeune, NC, in cooperation with Baker Environmental during 1997 and the first half of 1998. The Site 88 DNAPL zone was located at 17 to 20 ft bgs, both beneath and adjacent to Building 25, the Base dry-cleaning facility. In addition to the DNAPL zone, a zone of LNAPL has also been identified at a depth of approximately 7 to 10 ft bgs. This LNAPL zone is contaminated with Varsol™, a petroleum distillate that was used as the dry-cleaning solvent before it was replaced by PCE in the 1970s.

The shallow aquifer containing the PCE DNAPL zone is composed of fine sand and silt with an average hydraulic conductivity of approximately 5×10^{-4} cm/s (~1.4 ft/day). The sediments grade finer at the base of the aquifer to a clayey silt immediately above the clay aquitard; this basal silt layer was measured to have a hydraulic conductivity of about 1×10^{-4} cm/s (~0.3 ft/day). The clay aquitard, at the base of the shallow aquifer, appears to provide effective protection against further downward migration of DNAPL contamination to the underlying Castle Hayne Aquifer. The equivalent pressure for entry of DNAPL into the clay aquitard was measured to be approximately 15 ft of DNAPL head. The hydraulic head drop across the aquitard from the shallow aquifer to the Upper Portion of the Castle Hayne is of the order of 7 ft.

The DNAPL zone extends laterally in the shallow sand aquifer to approximately 20 to 30 ft north of Building 25 and is bounded below by the clay aquitard. The upper surface of the clay layer forms a stratigraphic trap (i.e., depression) in which some of the DNAPL has pooled. DNAPL saturations increase with depth from 17 to 20 ft bgs, with residual DNAPL grading downward to free-phase DNAPL above the clay surface. This free-phase DNAPL is, however, contained within clayey silts and the ability to recover DNAPL from this zone via traditional pumping from recovery wells is very limited.

A well field of three injection, six extraction, and two hydraulic control wells was installed for use in a partitioning interwell tracer test, or PITT, to measure the volume and spatial distribution of PCE DNAPL in the test zone. During the PITT, the tracers swept a pore volume of approximately 4,800 gallons of the shallow aquifer, in the depth interval between about 15 to 20 ft bgs. A UTCHEM-based geosystem model of the well field was developed for preliminary design of the PITT. The geosystem model was updated and calibrated based on the results of a conservative interwell tracer test (using bromide as a tracer). The updated/calibrated model was then used for further simulations to finalize the PITT design.

It was determined by partitioning tracer testing over a period of forty days in May-June 1998 that the DNAPL zone contained approximately 74-88 gallons of PCE DNAPL. Additional DNAPL is known to be present directly beneath Building 25, but that area

was not included in this DNAPL investigation because of potential operational conflicts with ongoing dry-cleaning activities. The average DNAPL saturations measured by the PITT ranged from approximately 4.5% adjacent to Building 25 and decreasing to 0.4% at a distance of 20 ft away from Building 25. It appears likely, however, that the low-level DNAPL contamination detected by the PITT in the test zone area away from the building (i.e., 0.4% DNAPL saturation) is actually the result of tracer sorption to natural organic matter (i.e. peat) in the sediments rather than partitioning to DNAPL. This conclusion is supported by column test results that were obtained prior to the PITT. Therefore, the area approximately 20 ft north of the building appears likely to be DNAPL free. The results of the SEAR demonstration will provide clarification for the presence or absence of DNAPL in this area of the test zone. Finally, the PITT data revealed an approximately four-fold decrease in effective permeability between the fine sands and basal silt zones in the test zone portion of shallow aquifer.

These results have several implications for the SEAR demonstration. Firstly, it shows that the geosystem model developed thus far is a reasonable representation of the contaminated DNAPL zone in the test area; corrections to accommodate potential biodegradation of injected chemicals as well as varying Varsol™ concentrations across the test zone will improve the model. Secondly, it illustrates that most of the PCE DNAPL is in the lower permeability (basal) zone of the aquifer, and that the remediation challenge will be to design the surfactant flood to effectively remove the DNAPL contamination from this zone. Finally, it indicates that there is some utility to including a non-alcohol based conservative tracer (e.g. bromide) in the tracer suite to examine the potential biodegradation of alcohol tracers during the final post-SEAR PITT.

Analytical difficulties were encountered during this PITT that point to the need to address GC fouling by calcium chloride in order to obtain an accurate analysis of the SEAR and post-SEAR PITT samples.

Finally, the pre-SEAR PITT has provided valuable data for evaluating the baseline conditions within the test zone for SEAR test design. The data on the averaged DNAPL saturations, the DNAPL volume in the test zone, and the approximate DNAPL distribution will refine the existing site geosystem model for optimum SEAR design.

13.0 REFERENCES

Annable M.D., P.S.C. Rao, K. Hatfield., W.D. Graham., A.L. Wood and C.G. Enfield, 1998. Partitioning Tracers for Measuring Residual NAPL: Field Scale Test Results. *J Env. Eng*., June, 1998, pp.498-503.

Baker Environmental. 1996. "Phase I Investigation Report, Operable Unit No. 15 (Site 88), Marine Corps Base Camp Lejeune, North Carolina"; prepared for the Naval Facilities Engineering Command, Atlantic Division (LANTDIV).

Baker, 1997. Dense Nonaqueous Phase Liquid Investigation Summary Report, Operable Unit No. 15 (Site 88), Marine Corps Base MCB Camp Lejeune, North Carolina. Report prepared for the Dept of the Navy Atlantic Division, Naval Facilities Engineering Command, Norfolk, Virginia, September 15, 1997.

Baker, 1998a. Focused Remedial Investigation Report, Operable Unit No. 15 (Site 88), Marine Corps Base Camp Lejeune, North Carolina. Report prepared for the Dept of the Navy Atlantic Division, Naval Facilities Engineering Command, Norfolk, Virginia, May 15, 1997.

Baker, 1998b. Varsol Investigation Summary Report, Operable Unit No. 15 (Site 88), Marine Corps Base Camp Lejeune, North Carolina. Report prepared for the Dept of the Navy Atlantic Division, Naval Facilities Engineering Command, Norfolk, Virginia, March 20, 1998.

Broholm K, and S. Feenstra, 1995. Laboratory Measurements of the Aqueous Solubility of Mixtures of Chlorinated Solvents. *Environ Toxicol Chem*, (14)1, pp. 9-15.

Caughey, M.E., M.J. Barcelona, R.M. Powell, R.A. Cahill, C. Gron, D. Lawrenz, and P.L. Meschi, 1995. Interlaboratory Study of a Method for Determining Nonvolatile Organic Carbon in Aquifer Materials. *Environmental Geology*, v.26, pp. 211-219.

Cayais, J.L., R.S. Schechter and W.H. Wade, 1975. The Measurement of Low Interfacial Tension Via the Spinning Drop Technique. In: Adsorption at Interfaces, ACS Symposium series, 8, J.R. Gould (ed), American Chemical Society, Washington D.C., pp. 234.

Datta Gupta, A., G. A. Pope, and R. L. Thrasher, 1986. A Symmetric, Positive Definite Formulation of a Three-Dimensional Micellar/Polymer Simulator. *SPE Reser. Eng*., 1(6), p622.

Delshad, M., G.A. Pope, and K. Sepehrnoori, 1996. A Compositional Simulator for Modeling Surfactant-Enhanced Aquifer Remediation: 1. Formulation. *J. Contaminant Hydrology,* v23, pp. 303-327.

Demond, A.H. and A.S. Lindner, 1993. Estimation of Interfacial Tension Between Organic Liquids and Water. *Environmental Science & Technology*, (27)12, pp. 2318-2331.

DE&S, 1998. Demonstration of Surfactant-Enhanced Aquifer Remediation of Chlorinated Solvent DNAPL at Operable Unit 2, Hill AFB, Utah. Prepared for the Air Force Center for Environmental Excellence Technology Transfer Division, Brooks Air Force Base, Texas, and OO-ALC/EMR, Hill Air Force Base, Ogden Utah, January 1998. Duke Engineering & Services, Austin, Texas.

DE&S, May 1998a. Work Plan for a Partitioning Interwell Tracer Test Site 88 Marine Corps Base Camp Lejeune, North Carolina. Duke Engineering & Services, Austin, Texas.

DE&S, May 1998b. Sampling and Analysis Plan for a Partitioning Interwell Tracer Test, Site 88 Marine Corps Base Camp Lejeune, North Carolina. Duke Engineering & Services, Austin, Texas.

Dwarakanath, V. and G.A. Pope, 1998. A New Approach for Estimating Alcohol Partition Coefficients between Nonaqueous Phase Liquids and Water. *Environmental Science and Technology*, 32(11) pp.1662-1666.

Edgar, J., 1997. MS Thesis, The University of Texas at Austin.

Environmental Protection Agency, 1992. Estimating Potential for Occurrence of DNAPL at Superfund Sites. Publication 9355.4-07FS, Office of Solid Waste and Emergency Response (OSWER), Washington D.C. January 1992.

Freeze, R.A., and J.A. Cherry, 1979. *Groundwater*, Prentice-Hall, Englewood Cliffs, NJ, 604 pp.

INTERA, 1997. Demonstration of Surfactant-Enhanced Aquifer Remediation of Chlorinated Solvent DNAPL At Operable Unit 2, Hill AFB, Utah. Prepared for the Air Force Center for Environmental Excellence, Technology Transfer Division, Brooks Air Force Base, San Antonio, Texas, Draft. Duke Engineering & Services (formerly INTERA), Austin, Texas.

Jin, M., M. Delshad, V. Dwarakanath, D.C. McKinney, G.A. Pope, K. Sepehrnoori, C.E. Tilford, and R.E. Jackson, 1995. Partitioning Tracer Test for Detection, Estimation and Remediation Performance Assessment of Subsurface Nonaqueous Phase Liquids. *Water Resources Research,* (31)5, pp. 1201-1211.

Jin, M., 1995. Surfactant-Enhanced Remediation and Interwell Partitioning Tracer Test for Characterization of NAPL Contaminated Aquifers. Ph.D. Dissertation, University of Texas at Austin.

Jin, M., Jackson, R.E., Pope, G.A., and S. Taffinder, 1997. Development of Partitioning Tracer Tests for Characterization of Nonaqueous-Phase Liquid-Contaminated Aquifers. SPE 39293. Presented at the SPE 72nd Annual Technical Conference & Exhibition held in San Antonio, Texas, 5-8 October 1997.

Jin, M., Butler, G.W., Jackson, R.E., Mariner, P.E., Pickens, J.F., Pope, G.A., Brown, C.L., and D.C. McKinney, 1997b. Sensitivity Models and Design Protocol for Partitioning Tracer Tests in Alluvial Aquifers. *Ground Water, v.35, no.6, pp 964-972.*

Jin, M. and G. Pope, 1998. The Interpretation and Error Analysis of Partitioning Interwell Tracer Test Data. submitted for publication to *Environmental Science & Technology*

Mackay, D.M. and J.A. Cherry, 1989. Groundwater Contamination: Pump-and-Treat Remediation. *Environmental Science & Technology, v.23, no.6, pp.630-636.*

Mariner, P.E., M. Jin, and R.E. Jackson, 1997. An Algorithm for the Estimation of NAPL Saturation and Composition from Typical Soil Chemical Analyses. *Ground-Water Monitoring and Remediation*, v.17, no. 2, pp. 122-129.

Neuman, S.P., 1975. Analysis of Pumping Test Data from Anisotropic Unconfined Aquifers Considering Delayed Yield. *Water Resources Research*, vol. 11, no. 2, pp. 329-342.

Pope, G.A. and R.C. Nelson, 1978. A Chemical Flooding Compositional Simulator. *SPE J*. 18(5), p339.

Pope, G.A., M. Jin, V. Dwarakanath, B. Rouse, and K. Sepehrnoori, 1994. Partitioning Tracer Tests to Characterize Organic Contaminants. In: Proceedings of the 2nd Tracer Workshop, University of Texas at Austin, November 14th & 15th, 1994.

Pope, G.A. and W.H. Wade, 1995. Lessons from enhanced oil recovery research for surfactant enhanced aquifer remediation. In: Sabatini, D.A., Knox, R.C., Harwell, J.H. (Eds.), Surfactant-Enhanced Subsurface Remediation Emerging Technologies, ACS symposium series 594, American Chemical Society, Washington, DC, 142-160.

Rice University, INTERA, University of Texas at Austin, and Radian, 1997. Surfactant/Foam Process for Aquifer Remediation – Draft Final. Prepared for the Advanced Applied Technology Demonstration Facility, Rice University, Houston, Texas. November.

Saad, N., G.A. Pope, and K. Sepehrnoori, 1990. Application of Higher-Order Methods in Compositional Simulation. *SPE Reser. Eng*. 5(4), p623.

Schwarzenbach, R.P and J. Westall, 1981. Transport of Nonpolar Organic Compounds from Surface Water to Groundwater; Laboratory Sorption Studies. *Environmental Science and Technology*, v.15, p.1360.

Taylor, J.R., 1997. *An Introduction to Error Analysis*, second edition, University Science Books, Sausalito, Calif.

West C.C., 1992. Surfactant-Enhanced Solubilization of Tetrachloroethylene and Degradation Products in Pump and Treat Remediation. In: *Transport and Remediation of Subsurface Contaminants*, edited by Sabatini, D. and R.C. Knox, ACS Symp Series 491, ACS Washington DC, pp. 149-158).

Young, C.M., R.E. Jackson, M. Jin, J.T. Londergan, P.E. Mariner, G.A. Pope, F.J. Anderson, and T. Houk, 1999. Characterization of a TCE DNAPL Zone in Alluvium by Partitioning Tracers. Accepted for publication by Ground Water Monitoring and Remediation, Winter Issue, v. XIX, no. 1, pp 84-94.