

DRAFT
Treatability Study in Support of
Intrinsic Remediation for
IRP Site SS-16

Volume 1 - Report



Langley Air Force Base
Hampton, Virginia

Prepared For

Air Force Center for Environmental Excellence
Technology Transfer Division
Brooks Air Force Base
San Antonio, Texas

and

1 CES/CEVR
Langley Air Force base
Hampton, Virginia

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DRAFT
TREATABILITY STUDY IN SUPPORT OF
INTRINSIC REMEDIATION FOR
IRP SITE SS-16

VOLUME 1 - REPORT

at

LANGLEY AIR FORCE BASE
HAMPTON, VIRGINIA

August 1996

Prepared For

AIR FORCE CENTER FOR ENVIRONMENTAL EXCELLENCE
TECHNOLOGY TRANSFER DIVISION
BROOKS AIR FORCE BASE
SAN ANTONIO, TEXAS

and

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LANGLEY AIR FORCE BASE
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environment. The Bioplume II model was used to estimate the rate and direction of dissolved BTEX movement through the shallow groundwater under the influence of advection, dispersion, sorption, and biodegradation. Input parameters for the Bioplume II model were obtained primarily from data collected by Parsons ES, supplemented with existing site characterization data. Model parameters that were not measured at the site were estimated using reasonable literature values.

The results of this demonstration suggest that natural attenuation of BTEX contamination in shallow groundwater will be sufficient to ensure protection of human health and the environment at present and in the future. Dissolved BTEX concentrations in excess of federal drinking water standards may persist at the site for approximately 40 years however, model results suggest that the dissolved BTEX plume will not migrate downgradient of the site during this time. The Air Force therefore recommends intrinsic remediation with LTM as the most appropriate remedial action to address dissolved BTEX contamination in groundwater at IRP Site SS-16.

To verify the Bioplume II model predictions, and to ensure that the selected technology is meeting objectives, the Air Force recommends using 8 LTM wells and 3 point-of-compliance (POC) wells to monitor the long-term migration and degradation of the dissolved BTEX plume. These wells should be sampled annually for 10 years, with the need for additional sampling and the appropriate sampling interval reevaluated at that time. Along with other analyses used to verify the effectiveness of intrinsic remediation, the groundwater samples should be analyzed for BTEX compounds by US Environmental Protection Agency Method SW8020. If BTEX concentrations in groundwater from the POC wells exceed the applicable federal drinking water standards, additional engineered controls to augment the beneficial effects of intrinsic remediation could be required to ensure protection of human health and the environment.

SECTION 1 INTRODUCTION

This report was prepared by Parsons Engineering Science, Inc. (Parsons ES) and presents the results of a treatability study (TS) conducted to evaluate the use of intrinsic remediation for remediation of fuel-hydrocarbon-contaminated groundwater at Installation Restoration Program (IRP) Site SS-16 (a former military gasoline service station site) at Langley Air Force Base (AFB, the Base), in Hampton, Virginia. Previous investigations determined that fuel hydrocarbons had been released into the soil and shallow groundwater at the site.

The main emphasis of the work described herein was to evaluate if naturally occurring attenuation mechanisms would be sufficient to reduce dissolved fuel-related compounds in groundwater to levels that meet state-specified groundwater protection standards. This study is not intended to be a contamination assessment report or a remedial action plan; rather, it is provided for the use of the Base and its prime environmental contractor(s) as information to be used for future decision making regarding this site.

As used throughout this report, the term "intrinsic remediation" refers to a management strategy that relies on natural physical, chemical, and biological mechanisms to control exposure of potential receptors to concentrations of contaminants in the subsurface that exceed regulatory levels intended to be protective of human health and the environment. These mechanisms include the processes of sorption, dispersion, and biodegradation, which facilitate intrinsic remediation of a variety of anthropogenic chemicals.

EXECUTIVE SUMMARY

This report presents the results of a treatability study (TS) performed by Parsons Engineering Science, Inc. (Parsons ES) at IRP Site SS-16, Langley Air Force Base, Virginia to evaluate the use of intrinsic remediation with long-term monitoring (LTM) as a remedial option for dissolved benzene, toluene, ethylbenzene, and xylenes (BTEX) contamination in the shallow aquifer. In addition to dissolved BTEX in the groundwater, residual light non-aqueous phase liquid (LNAPL) is present within the soil. Mobile LNAPL was not observed within the soil or at the water table during the field investigation. This study focused on the impact of residual LNAPL and dissolved BTEX on the shallow groundwater system at the site. Site history and the results from a previous soil and groundwater investigation also are summarized in this report.

Comparison of BTEX, electron acceptor, and biodegradation byproduct isopleth maps for IRP Site SS-16 provides strong qualitative evidence of biodegradation of BTEX compounds in the shallow groundwater. Geochemical data strongly suggest that biodegradation of fuel hydrocarbons is occurring at the site via aerobic respiration and the anaerobic processes of iron reduction, denitrification, sulfate reduction, and methanogenesis. Patterns observed in the distribution of hydrocarbons, electron acceptors, and biodegradation byproducts further indicate that biodegradation is reducing dissolved BTEX concentrations in site groundwater.

An important component of this study was an assessment of the potential for contamination in groundwater to migrate from the source area to potential receptors at concentrations above regulatory levels intended to be protective of human health and the

- Determining if naturally occurring processes of contaminant attenuation and destruction are occurring in groundwater at the site;
- Simulating the fate and transport of fuel hydrocarbons [benzene, toluene, ethylbenzene, and xylenes (BTEX)] in groundwater under the influence of advection, dispersion, adsorption, and biodegradation using the Bioplume II model;
- Evaluating a range of model input parameters to determine the sensitivity of the model to those parameters and to consider several contaminant fate and transport scenarios;
- Determining if naturally occurring processes are sufficient to minimize BTEX plume expansion so that groundwater quality standards can be met at a downgradient point of compliance (POC);
- Developing remedial action objectives (RAOs) and reviewing available remedial technologies;
- Using the results of modeling to recommend the most appropriate remedial option based on specific effectiveness, implementability, and cost criteria; and
- Providing a long-term monitoring (LTM) plan that includes LTM and POC well locations and a sampling and analysis plan.

Site characterization activities in support of this intrinsic remediation TS, performed in July 1995, included use of the Geoprobe® system for soil sample collection and monitoring point installation; aquifer testing; and sampling and analysis of groundwater from newly installed monitoring points and existing monitoring wells.

Site-specific data were used to develop a fate and transport model for the site using the groundwater flow and solute transport model Bioplume II, and to conduct a preliminary exposure pathways analysis. The Bioplume II model was used to simulate the movement of dissolved BTEX in the shallow saturated zone under the influence of advection, dispersion, sorption, and biodegradation. Model results were used to help assess the potential for completion of receptor exposure pathways involving groundwater, and to identify whether intrinsic remediation with LTM is an appropriate and defensible remedial option for contaminated groundwater.

Much of the hydrogeologic and groundwater chemical data necessary to evaluate the various remedial options was not available from previous investigations conducted at this site. The field work conducted under this program was oriented toward the collection of supplementary hydrogeologic and chemical data necessary to determine the extent of fuel-hydrocarbons in soil and groundwater, and to document and model the effectiveness of intrinsic remediation with LTM for fuel-hydrocarbon-contaminated groundwater.

This report contains nine sections, including this introduction, and six appendices. Section 2 summarizes site characterization activities. Section 3 summarizes the physical characteristics of the study area. Section 4 describes the nature and extent of soil and groundwater contamination and the geochemistry of soil and groundwater at the site. Section 5 describes the Bioplume II model and design of the conceptual model for the site, lists model assumptions and input parameters, and describes sensitivity analyses, model output, and the results of the Bioplume II modeling. Section 6 develops and presents a limited comparative analysis of remedial alternatives. Section 7 presents the LTM plan for the site, and Section 8 presents the conclusions of this work. Section 9 lists the references used to develop this document. Appendix A contains pertinent figures and tables containing data collected during the previous site investigation [Water and Air Research, Inc (WAR), 1982; Radian Corporation and Law Environmental Services (Radian and Law), 1993; Radian and Law, 1995]. Appendix B contains Geoprobe® borehole logs, monitoring point installation, development and sampling records, slug test results, and survey data. Appendix C presents soil and groundwater analytical results. Appendix D contains calculations and model input parameters, and Appendix E contains Bioplume II model input and output in American standard code for information interchange (ASCII) format on a diskette. Appendix F contains remedial alternative design and cost calculations.

1.2 FACILITY AND SITE BACKGROUND

Langley AFB is located in Hampton City in southeastern Virginia. The Base covers approximately 2,900 acres and is located within the outer coastal plain physiographic province of Virginia (Figure 1.1). The Base is bordered by the city of Hampton on the south, the city of Poquoson on the north, and the city of Newport News approximately one mile to the west. Norfolk is approximately 12 miles south-southeast of the Base. The Back River forms the northeastern and southeastern borders of the Base and discharges into Chesapeake Bay, approximately 3 miles east of the Base. Predominant land uses outside of Langley AFB are residential, light industrial, and commercial.

Langley Field, the predecessor of Langley AFB, became operational in 1917. The mission of Langley Field varied throughout its period of operation. Langley Field officially became Langley AFB in January of 1948, shortly after the formation of the US Air Force (USAF) Tactical Air Command (TAC) at the Field. Langley AFB became the headquarters for the USAF Air Combat Command (ACC) in June 1992, after the TAC was inactivated during USAF restructuring (USAF, 1993). The 1st Fighter Wing under the ACC is the host unit at Langley AFB. The primary mission of the Wing is to maintain rapid combat capability for rapid global deployment to conduct air superiority operations (USAF, 1994). Approximately 9,000 permanent military personnel are assigned to Langley AFB, and about 3,000 civilians are employed at the Base (USAF, 1993).

IRP Site SS-16 (the Site) is located in the southeastern portion of the Base between Buildings 590 and 596 in an asphalt-paved parking lot (Figures 1.2 and 1.3). The following site history information was reported in a work plan prepared by Radian and Law in January 1993. The site was identified as an area of suspected fuel contamination during an IRP record search conducted by CH2M Hill in 1981. The suspected sources of contamination at the site include several former underground storage tanks (USTs) used

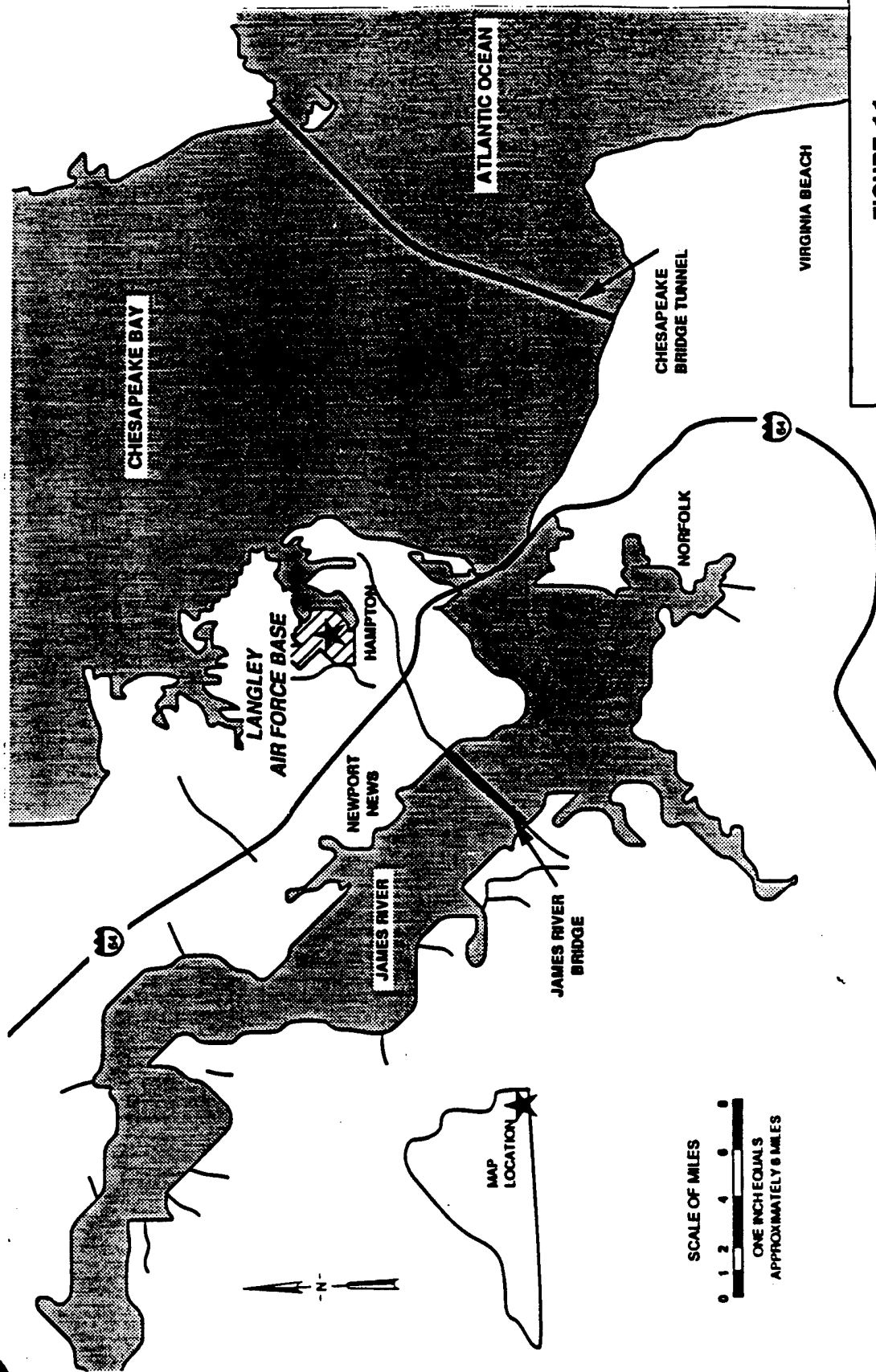


FIGURE 1.1

BASE LOCATION MAP

IRP SITE SS-16
INTRINSIC REMEDIATION TS
LANGLEY AFB, VIRGINIA



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ATLANTA, GEORGIA

SOURCE: LAW, 1991.

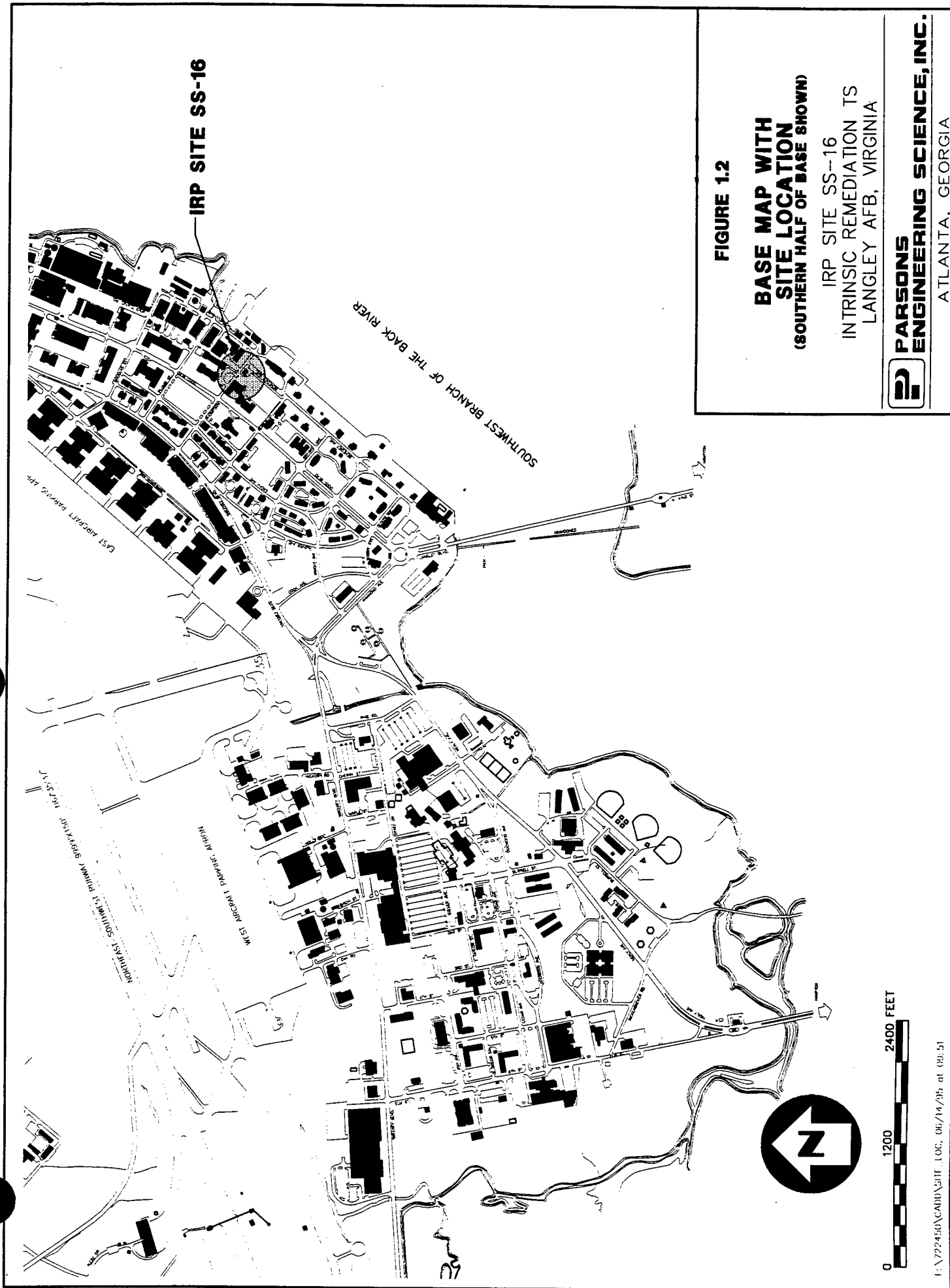


FIGURE 1.2

**BASE MAP WITH
SITE LOCATION
(SOUTHERN HALF OF BASE SHOWN)**

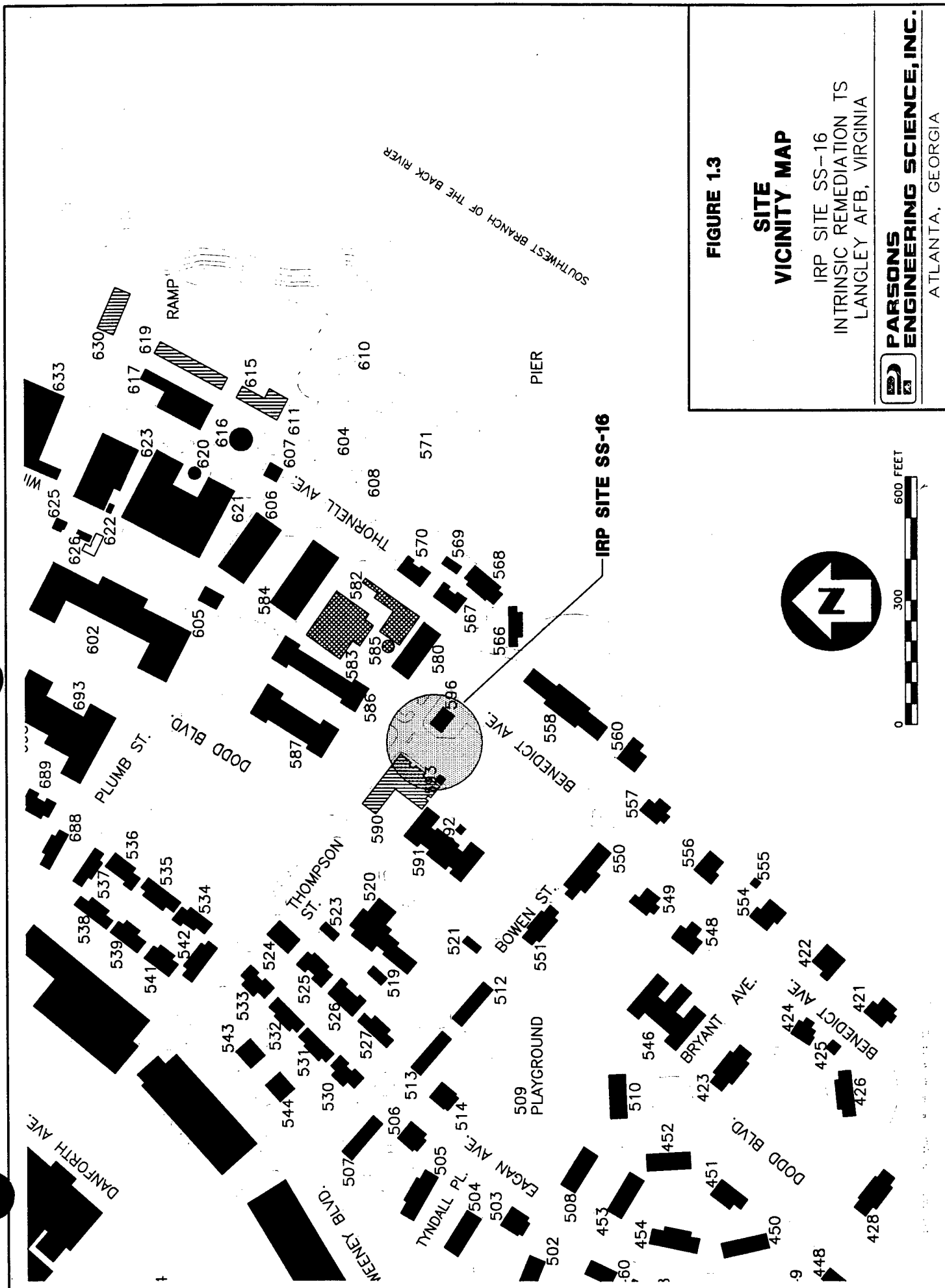
IRP SITE SS-16
INTRINSIC REMEDIATION TS
LANGLEY AFB, VIRGINIA



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ATLANTA, GEORGIA



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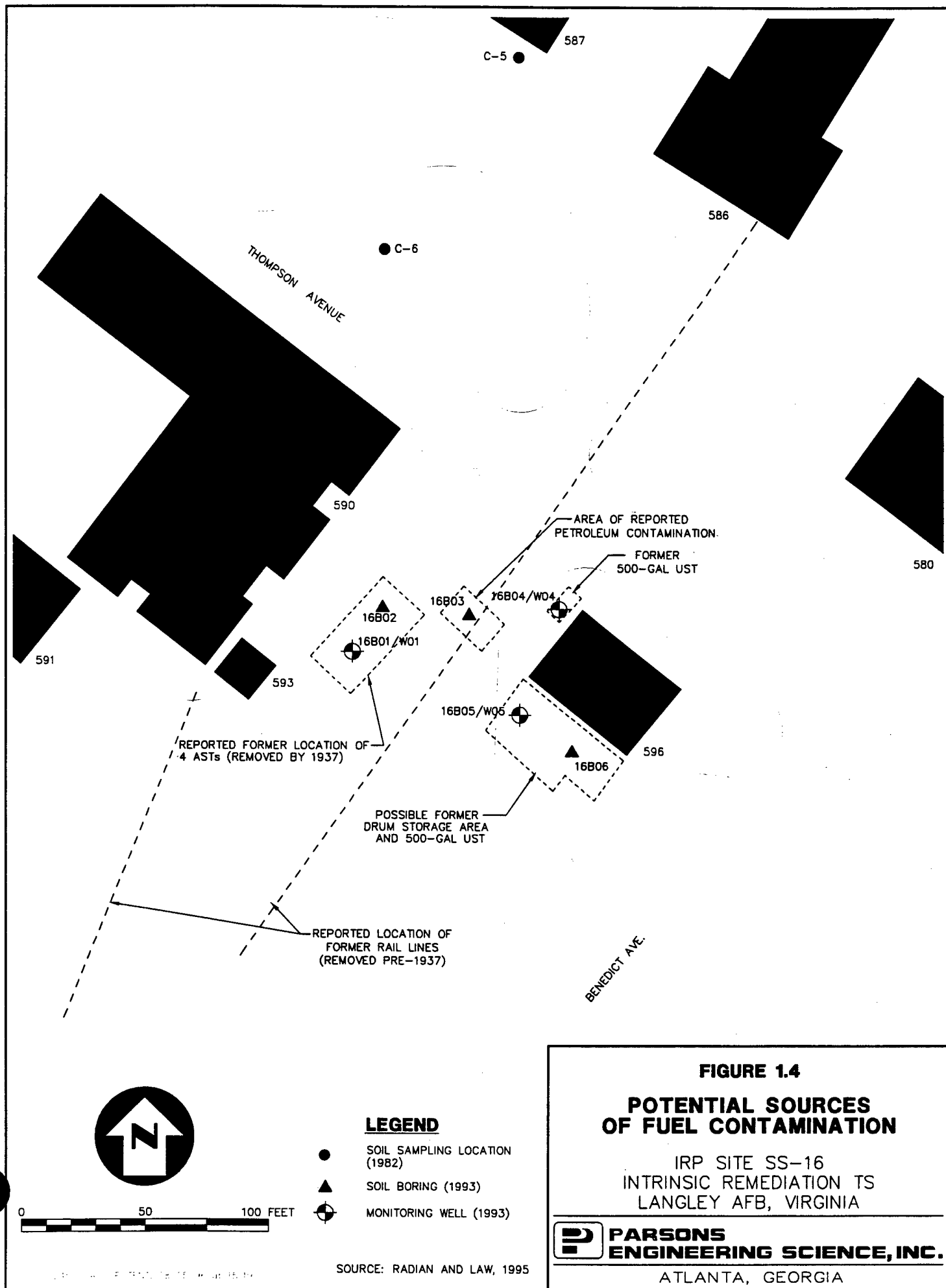


to store fuel oil at a former service station. These USTs were 550 gallons in size and were reportedly removed (date unknown). Analysis of historic aerial photographs taken in the 1930s and 1940s indicated that a structure, which was possibly a gasoline service station, was located near the present location of Buildings 590 and 596. A photograph from 1932 also showed that four aboveground storage tanks (ASTs) (contents unknown) and a possible drum storage area were located in the area (Figure 1.4). These ASTs were reportedly removed by 1937. A railroad track running through the area also was identified in the 1932 photograph and was reportedly removed by 1937. As reported by Radian and Law (1993), an architectural survey indicated that Building 596 was a gasoline service station and oil house when it was first constructed in the 1930s.

IRP Site SS-16, referred to as Area 16, was recognized as an area of suspected fuel contamination during a Phase I record search, which identified 12 areas of potential contamination at the Base (Radian and Law, 1993). In response to the Phase I investigation, a Phase II - Field Confirmation Study was conducted by WAR in 1982 to determine the presence or absence of contamination in these 12 areas. At Area 16, soil samples collected from two shallow corings indicated the presence of fuel contamination in the soil. However, based on the available site history, these samples may have been collected from an area away from the site (see Figure 1.4).

In 1991, fuel-product-stained soils were discovered at depths of up to 3 feet below ground surface (bgs) during excavation activities performed between Buildings 590 and 596.

In 1993, a site investigation was conducted by Radian and Law to determine the presence or absence of contamination in soil and groundwater at the site. Six borings were installed to groundwater. Three of the six borings were completed as monitoring wells (Figure 1.4). At the time of this writing, the investigation results report was in



preparation and few results were available. The available information indicated that at a minimum, arsenic was detected in soil, and benzene was detected in the shallow groundwater at the site (Radian and Law, 1995).

SECTION 2

SITE CHARACTERIZATION ACTIVITIES

This section presents the methods used by Parsons ES personnel to collect site-specific data at IRP Site SS-16 a former military gasoline service station site, Langley AFB, Virginia. To meet the requirements of the intrinsic remediation demonstration, additional data were required to evaluate near-surface geology and geochemistry, aquifer properties, and the extent of soil and groundwater contamination. Site characterization activities involved using a Geoprobe® for soil sampling and groundwater monitoring point placement. Previous investigations conducted at the site utilized standard hollow-stem auger (HSA) drilling and soil sampling as well as sampling of groundwater at three monitoring wells (Figure 1.4). Groundwater sampling was accomplished during this investigation at newly installed monitoring points and the pre-existing monitoring wells. Aquifer slug tests were conducted at the three monitoring wells.

The physical and chemical data listed below were collected during the field work phase of the TS:

- Depth from measurement datum to the water table or potentiometric surface in monitoring wells and monitoring points;
- Stratigraphy of subsurface media;
- Hydraulic conductivity as determined from slug test data;
- Groundwater geochemical data [pH, temperature, total alkalinity, oxidation/reduction potential (ORP), dissolved oxygen (DO), chloride, nitrate, nitrite, ammonia, ferrous and total iron, sulfate, manganese, ammonia, carbon dioxide, and methane];

- Concentrations of aromatic volatile organic compounds (VOCs), total volatile (gasoline-range) petroleum hydrocarbons (TVH), total extractable hydrocarbons as diesel (TEH), and arsenic in groundwater; and
- Concentrations of aromatic VOCs, TVH, TEH, total organic carbon (TOC), moisture, and arsenic in soil.

The following subsections describe the procedures that were followed when collecting site-specific data. Additional details regarding investigative activities are presented in the work plan (Parsons ES, 1995).

2.1 DRILLING, SOIL SAMPLING, AND MONITORING POINT INSTALLATION

Geoprobe®-related field work occurred between July 11 and July 18, 1995, and consisted of soil sampling and groundwater monitoring point installation for monitoring points 16MP-1 through 16MP-22. The term "monitoring point" is used in this report to distinguish these groundwater monitoring stations from conventionally constructed monitoring wells. These activities were performed according to the procedures described in the work plan (Parsons ES, 1995) and summarized in the following paragraphs.

The Geoprobe® system is a hydraulically powered percussion/probing machine used to advance sampling tools through unconsolidated soils. This system provides for the rapid collection of soil, soil gas, and groundwater samples at shallow depths while minimizing the generation of investigation-derived waste materials. Figure 2.1 is a diagram of the Geoprobe® system.

2.1.1 Groundwater Monitoring Point Locations and Completion Intervals

Twenty-two new groundwater monitoring points were installed at 20 locations to assist in the characterization of the contaminant distribution and the shallow groundwater flow system at IRP Site SS-16. These points are identified as 16MP-1 through 16MP-22. The new monitoring points were installed at the locations shown on Figure 2.2. Table 2.1 presents completion details. Nested points (e.g., 16MP-13/16MP-22 and

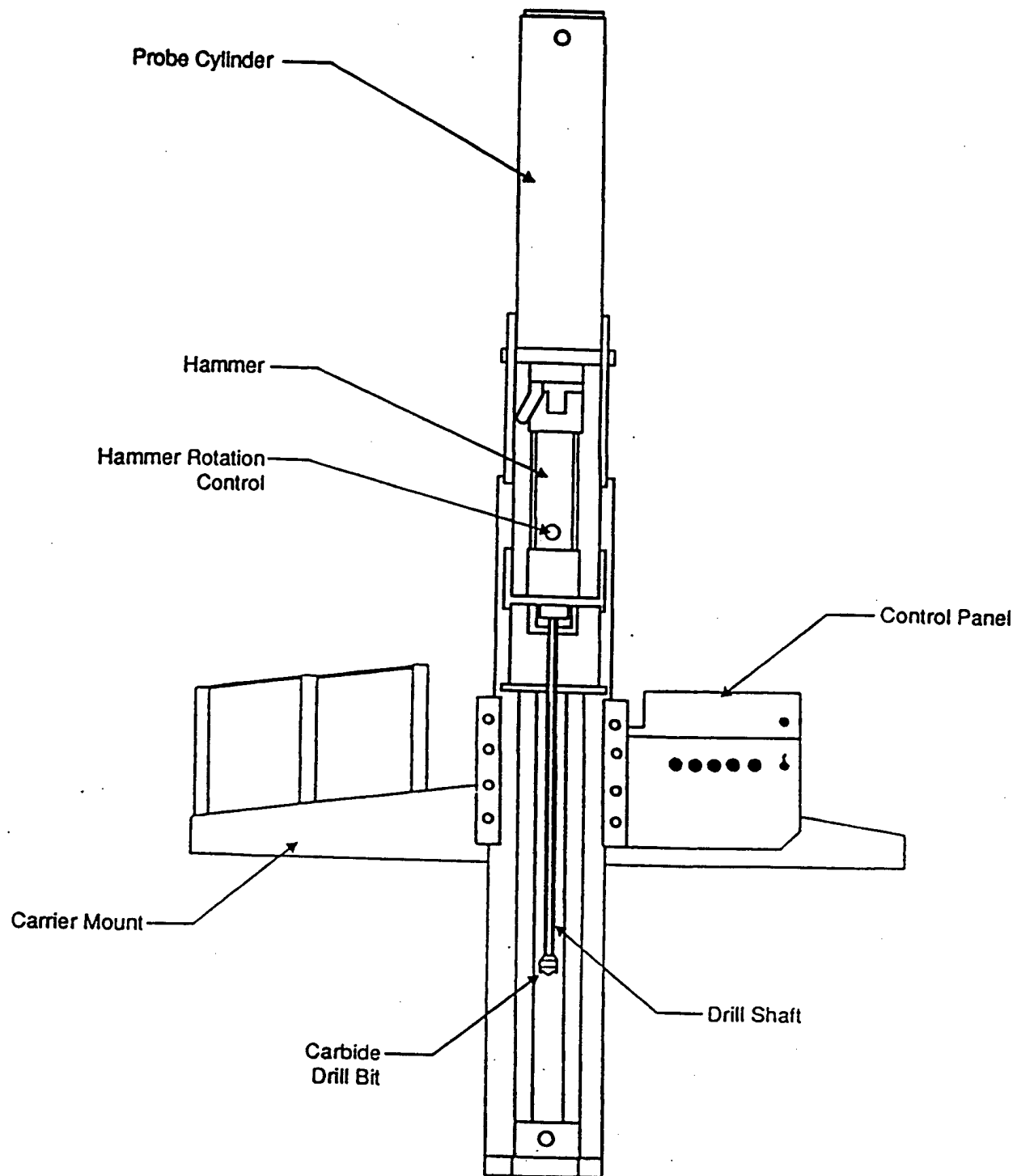


FIGURE 2.1

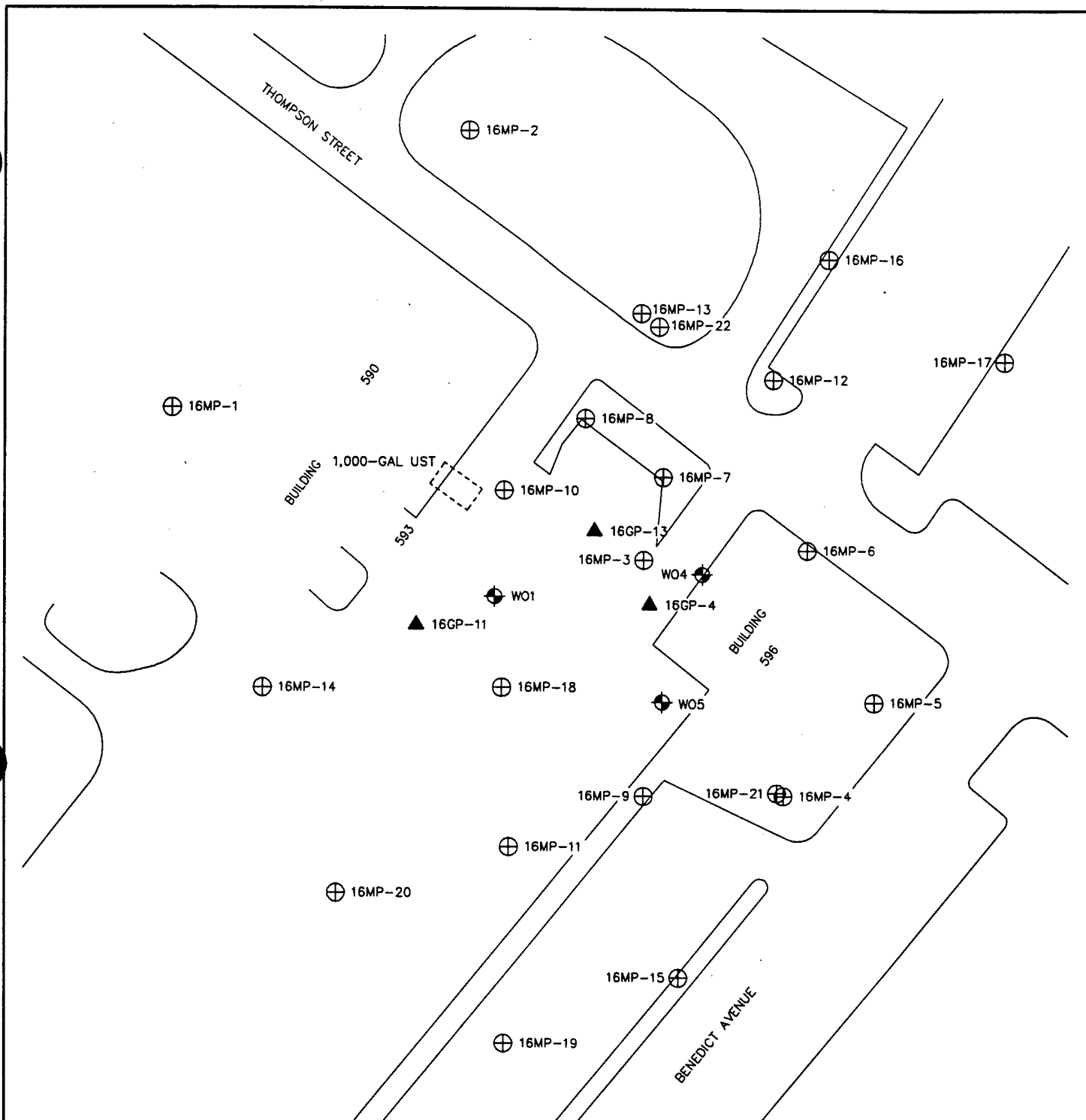
**CROSS-SECTION
OF GEOPROBE**

IRP SITE SS-16
INTRINSIC REMEDIATION TS
LANGLEY AFB, VIRGINIA



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LEGEND

- W01 MONITORING WELL
- 16MP-10 MONITORING POINT
- 16GP-11 GEOPROBE BORING



0 50 100
SCALE (FEET)

1. CURRENT LADD WELL - 01.08.106.09 at 10.17

FIGURE 2.2

MONITORING POINT LOCATIONS

IRP SITE SS-16
INTRINSIC REMEDIATION TS
LANGLEY AFB, VIRGINIA



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TABLE 2.1
BORING, MONITORING POINT, AND WELL COMPLETION DATA
IRP SITE SS-16
INTRINSIC REMEDIATION TS
LANGLEY AFB, VIRGINIA

Boring/ Point/Well Identification	Installation Date	Northing (feet)	Easting (feet)	Well Diameter (inches)	Borehole Diameter (inches)	Total Depth (ft. bgs) ^a	Screened Interval (ft. bgs)	Elevation toc (ft. msl) ^b	Elevation Ground (ft. msl)
16GP-4	7/11/95	278388.92	2628587.99	NA	2	8.0	NA	NA	7.4
16GP-11	7/13/95	278381.48	2628506.85	NA	1	10.0	NA	NA	8.2
16GP-13	7/13/95	278414.44	2628568.83	NA	2	8.0	NA	NA	7.7
16MP-1	7/11/95	278456.71	2628420.89	1.0	2	10.0	5.0-10.0	8.58	8.5
16MP-2	7/11/95	278552.97	2628525.00	0.5	2	9.0	4.0-9.0	7.90	7.7
16MP-3	7/11/95	278404.46	2628586.04	0.5	2	8.0	3.0-8.0	7.34	7.3
16MP-4	7/12/95	278322.06	2628635.00	1.0	2	8.0	3.0-8.0	7.91	7.8 ^c
16MP-5	7/12/95	278355.08	2628666.46	1.0	2	8.0	3.0-8.0	7.91	7.4
16MP-6	7/12/95	278407.98	2628643.18	0.5	2	10.0	5.0-10.0	6.85	6.7
16MP-7	7/12/95	278433.24	2628592.87	0.5	2	8.0	3.0-8.0	7.70	7.4
16MP-8	7/12/95	278453.47	2628565.52	1.0	2	8.0	3.0-8.0	7.79	7.6
16MP-9	7/13/95	278321.94	2628586.00	0.5	2	10.0	5.0-10.0	8.36	8.2
16MP-10	7/13/95	278428.35	2628537.29	0.5	2	8.0	3.0-8.0	7.98	8.0
16MP-11	7/14/95	278303.87	2628538.92	1.0	2	10.0	5.0-10.0	7.90	8.0
16MP-12	7/14/95	278467.16	2628631.34	1.0	2	10.0	5.0-10.0	7.64	7.3
16MP-13	7/14/95	278489.76	2628584.89	1.0	2	10.0	5.0-10.0	7.43	7.4
16MP-14	7/14/95	278359.62	2628452.71	1.0	1	10.0	5.0-10.0	8.09	8.1
16MP-15	7/15/95	278258.65	2628598.13	1.0	2	10.0	5.0-10.0	7.91	7.8
16MP-16	7/15/95	278508.86	2628650.59	1.0	2	10.0	5.0-10.0	7.68	7.5
16MP-17	7/15/95	278473.52	2628712.10	1.0	2	10.0	5.0-10.0	7.47	7.3
16MP-18	7/17/95	278359.95	2628536.40	1.0	1	9.5	4.5-9.5	7.93	7.9
16MP-19	7/17/95	278235.39	2628537.27	1.0	2	10.0	5.0-10.0	8.18	8.2
16MP-20	7/17/95	278287.67	2628478.63	1.0	2	10.0	5.0-10.0	8.20	8.2
16MP-21	7/18/95	278323.10	2628632.73	0.5	1	22.5	20.0-22.5	7.83	7.8
16MP-22	7/18/95	278489.35	2628585.32	0.5	2	22.5	20.0-22.5	7.19	7.4 ^d
W01	9/16/93	278391.49	2628534.07	2.0	8	13.6	3.0-13.0	7.98	8.1
W04	9/11/93	278399.60	2628606.55	2.0	8	13.6	3.0-13.0	7.17	7.3
W05	9/11/93	278355.16	2628592.51	2.0	8	13.6	3.0-13.0	7.83	7.9

a/ - ft. bgs = feet below ground surface.

b/ - toc = top of casing; ft. msl = feet above mean sea level.

c/ - inferred from ground elevation at MP-21.

d/ - inferred from ground elevation at MP-13.

16MP-4/16MP-21) were installed adjacent to each other, with one point screened across the water table, and the other point screened approximately 12 to 14 feet below the bottom of the shallow point. The monitoring point locations were selected to provide the hydrogeologic and chemical data necessary for successful implementation of the Bioplume II model and to support the intrinsic remediation demonstration.

2.1.2 Groundwater Monitoring Point Installation and Soil Sampling Procedures

2.1.2.1 Pre-Installation Activities

All subsurface utility lines or other man-made subsurface features were located, and proposed monitoring point locations were cleared and approved by the Base prior to any Geoprobe® activities. Water used in equipment cleaning or grouting was obtained from an onsite potable water supply.

2.1.2.2 Equipment Decontamination Procedures

Prior to arriving at the site and between each monitoring point location, all probe rods, tips, sleeves, pushrods, samplers, tools, and other downhole equipment were decontaminated using an Alconox® detergent and potable water solution followed by a high-pressure potable water wash. All equipment also underwent an additional rinse with isopropyl alcohol followed by a final rinse with deionized water.

During installation operations, the Geoprobe®, probe rods, and any downhole drilling and/or sampling equipment were decontaminated at an area designated by the Base. Water from decontamination operations was collected in a 40-gallon plastic tub. A headspace analysis of collected rinseate water was taken with a PID following each decontamination event. All rinseate water generated during decontamination operations had a headspace reading of less than 5 parts per million, volume per volume (ppmv) so, in keeping with the work plan (Parsons ES, 1995a), the water was disposed of onsite as specified by the Base.

Fuel, lubricants, and other similar substances were handled in a manner consistent with accepted safety procedures and standard operating practices. All well completion materials were factory sealed and were not stored near or in areas that could be affected by these substances.

2.1.2.3 Borehole Placement and Soil Sampling

Boreholes were advanced using the Geoprobe® method, and were continuously sampled to the total depth of the borehole. In a few instances, highly saturated sand below the water table prevented collection of continuous samples. A final borehole diameter of 2 inches was used for the installation of shallow and deep monitoring points with a 0.5- or 1-inch inside-diameter (ID) polyvinyl chloride (PVC) casing.

Continuous soil samples were obtained using a 1.5-inch-diameter by 4-foot-long stainless steel sampling barrel with a cutting shoe attached to the bottom. On some occasions, a 2-foot by 1-1/16-inch-ID sampler was used. The sampling barrel serves as both the driving point and the sample collection device, and is attached to the leading end of the probe rods. To collect a soil sample, the sampler was pushed or percussion driven to the desired sampling depth. The soil cores were retained within a clear acetate liner inside the sampling barrel. The probe rods were then retracted, bringing the sampling barrel to the surface. Soil samples were removed from the sampler as a composite of soil in 1-foot intervals within a sample liner, transferred to jars, and submitted to a laboratory for chemical analysis and/or geotechnical testing. In addition, a portion of the soil sample was placed in an unused, sealable plastic bag for PID headspace measurements of VOCs. Soil remaining in the liner was used for lithologic and stratigraphic logging. A new acetate liner was used each time a soil sample was collected.

Bags containing soil samples collected for the headspace screening procedure were quickly sealed and stored for 10 minutes at the ambient temperature. Semiquantitative

measurements were made by puncturing the bag seal with the PID probe and reading the concentration of the headspace gases. The PID relates the concentration of total VOCs in the sample to an isobutylene calibration standard. The PID was also used to monitor for VOCs in the worker breathing zone.

The Parsons ES field hydrogeologist observed Geoprobe® sampling and monitoring point installation activities and maintained a descriptive log of subsurface materials recovered. Final geologic borehole logs are presented in Appendix B. These logs contain:

- Sampled interval (top and bottom depth);
- Presence or absence of contamination based on odor, staining, and/or PID readings;
- Soil description, including color, major textural constituents, minor constituents, relative moisture content, grain size, structure or stratification, and any other significant observations; and,
- Lithologic contacts, with the depth of lithologic contacts and/or significant textural changes recorded to the nearest 0.1 foot.

Analyte-appropriate sample containers for the targeted analytes were provided by the subcontracted laboratory, Evergreen Analytical Laboratory, Inc. (EAL) of Wheatridge, Colorado. A sample label was attached to the container side, and the following information was legibly and indelibly written on the label:

- Sample identification;
- Sample depth;
- Sampling date; and,
- Sample collector's initials.

After the samples were sealed and labeled, they were placed in a cooler with ice and held for overnight transport via Federal Express® to EAL. A summary of the chemical analyses performed for soil and groundwater samples is presented in Table 2.2.

TABLE 2.2
ANALYTICAL PROTOCOL FOR
GROUNDWATER AND SOIL SAMPLES
IRP SITE SS-16
INTRINSIC REMEDIATION TS
LANGLEY AFB, VIRGINIA

MATRIX	METHOD	ANALYTICAL LABORATORY
WATER		
Total Iron	Colorimetric, Hach Method 8008	Field
Ferrous Iron (Fe+2)	Colorimetric, Hach Method 8146	Field
Ferric Iron (Fe+3)	Difference between total and ferrous iron	Field
Manganese	Colorimetric, Hach Method 8034	Field
Sulfate	Colorimetric, Hach Method 8051	Field
Sulfate	E300.0	EAL ^a
Nitrate	E300.0	EAL
Nitrite	E300.0	EAL
Redox Potential	Direct reading meter	Field
Oxygen	Direct reading meter	Field
pH	Direct reading meter	Field
Temperature	Direct reading meter	Field
Alkalinity (Carbonate [CO ₃ -2] and Bicarbonate [HCO ₃ -1])	Titrimetric, Hach Method 8221	Field
Carbon Dioxide	CHEMetrics Method 4500	Field
Chloride	E300.0	EAL
Ammonia--Diss. Gas in Water	CHEMetrics Method 4500, NH ₃	Field
Alkalinity	310.1	EAL
Methane	RSKSOP175	EAL
Aromatic Hydrocarbons (Including Trimethylbenzenes and Tetramethylbenzene)	SW8020 (RSKSOP-133)	EAL
Total Volatile Hydrocarbons	SW8015, modified	EAL
Total Extractable Hydrocarbons	SW8015, modified	EAL
Arsenic	AA, Furnace Technique	EAL
SOIL		
Total Organic Carbon	COU-02	EAL ^a
Moisture	E160.3	EAL
Aromatic Hydrocarbons	SW8020	EAL
Total Volatile and Extractable Hydrocarbons	SW8015, modified	EAL
Arsenic	SW7060, AA, Furnace Technique	EAL

a/ EAL = Evergreen Analytical laboratory, Inc. of Wheat Ridge, Colorado.

b/ Subcontracted by EAL to Huffman Laboratories of Golden Colorado.

Waste soils generated during monitoring point installation and sampling operations were screened for total VOCs with the PID by the headspace method. Soils with a PID reading of less than 10 ppm were spread on the ground surface in the vicinity of the site. Soils with a PID reading greater than 10 ppmv were placed in a 55-gallon drum located onsite, as directed by the Base.

2.1.3 Monitoring Point Installation

Groundwater monitoring points were installed in 22 boreholes under this program (Figure 2.2). Monitoring point installation procedures are described in the following paragraphs. Monitoring point completion diagrams are included in Appendix B.

2.1.3.1 Monitoring Point Materials Decontamination

Monitoring point completion materials were inspected by the field geologist and determined to be clean and acceptable prior to use. All monitoring point completion materials were factory sealed in plastic wrap. Pre-packaged casing, screen, and sand were used in point construction, and the bags were inspected for possible external contamination before use.

2.1.3.2 Monitoring Point Casing and Screen

Shallow monitoring points were constructed of Schedule 40 PVC riser pipe and screen having an ID of 0.5 or 1.0 inch. All casing and screen sections were flush threaded; glued joints were not used. The riser pipe at each monitoring point was fitted with a PVC top cap. A threaded PVC bottom cap was placed on the bottom of the screen. Monitoring point screens installed across the water table were 5 feet long and were factory slotted with 0.010-inch openings.

Deep monitoring points (16MP-21 and 16MP-22) were constructed using 0.5-inch-ID PVC. The monitoring point screens for the deep points were 2.5 feet long

and were factory slotted with 0.010-inch openings. The deep points were installed using the same procedures as the shallow points.

The field geologist verified and recorded the borehole depth, the lengths of all casing sections and tubing, and the depth to the top of all monitoring point completion materials placed in the annulus between the casing/tubing and borehole wall. All lengths and depths were measured to the nearest 0.1 foot.

2.1.3.3 Sand Filter Pack

Due to collapse of the sand borehole walls, a sand filter pack was not placed around the screened interval of each monitoring point. Therefore, the monitoring points were naturally sand-packed with the formation materials.

2.1.4 Monitoring Point Development

Prior to sampling, newly installed monitoring points were developed. Typically, development removes sediment from inside the well casing and flushes fines, cuttings, and drilling fluids from the sand pack and the portion of the formation adjacent to the well screen. Use of the Geoprobe® system to place monitoring points eliminates cuttings and drilling fluids. As a result, development of monitoring points was primarily intended to minimize the amount of fine sediment that might accumulate in the casing.

Development was accomplished using a peristaltic pump with dedicated silicon and high-density polyethylene (HDPE) tubing. The pump tubing was regularly lowered to the bottom of the shallow points so that fines were agitated and removed from the point in the development water. Development was continued until the fines in the point were removed and, the pH and temperature of the groundwater had stabilized. Headspace readings of the development waters were taken with a PID. Water with a headspace reading greater than 5 ppmv was collected in a 55-gallon steel drum. Water with a

headspace reading less than 5 ppmv was poured onto the ground in the immediate area around the point from which it originated.

2.2 GROUNDWATER SAMPLING

This section describes the procedures used for collecting groundwater quality samples. In order to maintain a high degree of quality control (QC) during this sampling event, the procedures described in the draft work plan (Parsons ES, 1995) and summarized in the following sections were followed.

Groundwater sampling occurred during July 1995, and consisted of collecting groundwater samples from monitoring points 16MP-1 through 16MP-20 and monitoring wells W01, W04, and W05. In addition to the sampling events conducted under this program, Radian and Law (1995) also have conducted groundwater sampling at the site.

2.2.1 Preparation and Equipment Cleaning

All equipment used for sampling was assembled and properly cleaned and calibrated (if required) prior to use in the field. All portions of sampling and test equipment that contacted the sample were thoroughly cleaned before use. This equipment included the water level probe and cable, equipment for measuring onsite groundwater chemical parameters, and other equipment that contacted the samples. The following cleaning protocol was used:

- Cleaned with potable water and phosphate-free laboratory-grade detergent;
- Rinsed with potable water;
- Rinsed with isopropyl alcohol;
- Rinsed with distilled or deionized water; and
- Air dried prior to use.

Any deviations from these procedures were documented in the field scientist's field notebook and on the groundwater sampling form.

As required, field analytical equipment was calibrated according to the manufacturers' specifications prior to field use. This requirement applied to direct-reading meters used for onsite chemical measurements of DO, pH, ORP, and temperature, as well as the Hach® meter used for other onsite geochemical analyses

2.2.2 Groundwater Sampling Procedures

Special care was taken to prevent contamination of the groundwater and extracted samples through cross-contamination from improperly cleaned equipment. Water level probes and cable used to determine static water levels and total well depths were thoroughly cleaned before and after field use and between uses at different sampling locations according to the procedures presented in Section 2.2.1. In addition, a clean pair of new, disposable latex gloves was worn each time a different well or monitoring point was sampled.

2.2.2.1 Water Level and Total Depth Measurements

Prior to removing any water from a monitoring point or well, the static water level was measured. In the shallow, 0.5 or 1.0-inch-diameter PVC monitoring points, an electrical water level probe was used to measure the depth to groundwater below the well datum to the nearest 0.01 foot. An oil/water interface probe capable of measuring the depth to both petroleum product (if present) and water was used in the previously installed 2-inch diameter wells. Free-phase hydrocarbons were not detected in any of the wells. After measurement of the static water level, the water level probe was lowered to the bottom of the well/point for measurement of total well depth (recorded to the nearest 0.01 foot). Based on these measurements, the volume of water to be purged from the wells/points was estimated.

2.2.2.2 Well/Monitoring Point Purging

Where possible, three times the calculated casing volume was removed from each well or monitoring point prior to sampling. Purging continued until the pH, DO

concentration, ORP, and temperature stabilized. A peristaltic pump with dedicated silicon and HDPE tubing was used for monitoring point evacuation. Headspace readings of the purge waters were taken with a PID. A decontaminated Teflon® bailer connected to a dedicated length of nylon rope was used to purge the monitoring wells. Water with a headspace reading greater than 5 ppmv was collected in a 55-gallon steel drum. Water with a headspace reading less than 5 ppmv was poured onto the ground in the immediate area around the point from which it originated.

2.2.2.3 Sample Collection

A peristaltic pump with dedicated silicon and HDPE tubing was used to extract groundwater samples from each monitoring point. A decontaminated Teflon® bailer connected to a dedicated length of nylon rope was used to extract groundwater samples from the three monitoring wells. Purging and sampling constituted one continuous sampling event. For shallow monitoring points, the dedicated HDPE tubing was lowered down the casing to the lower one-third of the screened interval. The samples were transferred directly into the appropriate sample containers. The water was carefully poured down the inner walls of each sample bottle to minimize aeration of the sample. Sample bottles for BTEX, TVH, methane, anions, alkalinity, VOCs, and Hach® field analyses were filled so that there was no headspace or air bubbles within the container. Table 2.2 lists the analyses performed on collected groundwater samples.

2.2.3 Onsite Chemical Parameter Measurement

2.2.3.1 Dissolved Oxygen Measurements

DO measurements were taken using a Yellow Springs Instrument (YSI) model 55 DO meter. Approximately 400 milliliters (mL) of purge water was placed into a 500-mL glass flask. The DO probe was then placed into this flask and swirled continuously. DO concentrations were recorded after the readings stabilized, and in all cases represent the lowest DO concentration observed.

2.2.3.2 pH and Temperature Measurements

Because the pH and temperature of the groundwater change significantly within a short time following sample acquisition, these parameters were measured in the field, in the same flask used for DO measurements. The measured values were recorded on the groundwater sampling record.

2.2.3.3 Hach® and CHEMetrics® Field Chemistry Measurements

An onsite laboratory staffed by Parsons ES personnel was established in Quseda Hall (Building 590) adjacent to the site and used to analyze for several indicator parameters in groundwater samples (Table 2.2). A Hach® DR/700 colorimeter was used to measure ferrous iron (Fe^{2+}), total iron ($\text{Fe}^{2+} + \text{Fe}^{3+}$), sulfate (SO_4^{2-}), and manganese (Mn^{2+}). Titrations using Hach® reagents were conducted to measure alkalinity [as milligrams per liter (mg/L) calcium carbonate (CaCO_3)]; and CHEMetrics® color tests were used to measure ammonia (NH_3) and carbon dioxide (CO_2). Groundwater samples were collected directly into clean glass containers, capped, and transported to the Parsons ES on-Base laboratory for analysis. Special care was taken to collect samples without headspace because headspace could influence the concentration of reduced species. The field holding time for each sample did not exceed 1 hour. Care also was taken to minimize sample temperature changes and exposure to sunlight. Concentrations of these indicator parameters were not quantitatively measured in soil samples.

2.2.4 Sample Handling

2.2.4.1 Sample Containers, Preservation, and Labels

The fixed-base analytical laboratory (EAL) provided sample containers, pre-preserved as appropriate.

The sample containers were filled as described in Section 2.2.2.3, and the container lids were tightly closed. The sample label was firmly attached to the container side, and the following information was legibly and indelibly written on the label:

- Facility name;
- Sample identification;
- Sample type (groundwater);
- Sampling date;
- Sampling time;
- Preservatives added; and
- Sample collector's initials.

2.2.4.2 Sample Shipment

After the samples were sealed and labeled, they were packaged for transport to EAL in Wheat Ridge, Colorado. The following packaging and labeling procedures were followed:

- Samples were packaged to prevent leakage or vaporization from the containers;
- Samples were cushioned to avoid breakage; and
- Ice was added to the shipping cooler to keep the samples cool.

The packaged samples were delivered by overnight courier (Federal Express®) to the laboratory. Chain-of-custody procedures outlined in the work plan (Parsons ES, 1995) were followed.

2.3 AQUIFER TESTING

Slug tests were performed in monitoring wells W01, W04, and W05 (Figure 2.2) to provide estimates of the hydraulic conductivity of the shallow saturated zone in the vicinity of IRP Site SS-16. Slug tests are single-well hydraulic tests used to estimate the hydraulic conductivity of an aquifer in the immediate vicinity of the tested well. Slug testing can be performed using either a rising head or a falling head test. Only rising head tests were used to determine hydraulic conductivity at this site. Detailed slug testing procedures are presented in the *Technical Protocol for Implementing Intrinsic Remediation with Long-Term Monitoring for Natural Attenuation of Fuel Contamination*

Dissolved in Groundwater (Wiedemeier *et al.*, 1995), hereafter referred to as the technical protocol document.

Data obtained during slug testing were analyzed using the computer program AQTESOLV® (Geraghty & Miller Modeling Group, 1994) and the methods of Bouwer and Rice (1976) and Bouwer (1989) for unconfined conditions. The results of slug testing are presented in Section 3.3.2.2 and Appendix B.

2.4 TIDAL INFLUENCE MONITORING

Tidal influence monitoring was conducted to determine if shallow groundwater flow beneath the site was influenced by tidal fluctuations in the nearby Back River. Water levels in the three monitoring wells and three monitoring points were measured over a period of 24 hours using a Hermit® 2000 Datalogger and pressure transducer system. Detailed tidal monitoring procedures are presented in the work plan (Parsons ES, 1995).

Data obtained during tidal influence testing were analyzed to determine the presence and magnitude of tidally influenced fluctuations in the monitored well and points. The results of tidal influence monitoring are presented in Section 3.3.2.5 and Appendix B.

2.5 SURVEYING

After completion of field work, the locations and elevations of all new monitoring points and previously-installed monitoring wells were surveyed by Miller-Stephenson & Associates, P.C. of Virginia Beach, Virginia. The horizontal locations and elevations of the measurement datum (top of PVC well/point casing) and the ground surface adjacent to the well casing were measured relative to existing on-Base survey control points. Horizontal locations were surveyed to the nearest 0.1 foot. Measurement datum elevations were surveyed to the nearest 0.01 foot. Ground surface elevations were surveyed to the nearest 0.1 foot. Survey data are presented in Table 2.1 and Appendix B.

SECTION 3

PHYSICAL CHARACTERISTICS OF THE STUDY AREA

This section incorporates data collected by Parsons ES in July 1995 and information presented by WAR (1982) and Radian and Law (1995). Investigative techniques used to determine the physical characteristics of the site are discussed in Section 2.

3.1 SURFACE FEATURES

3.1.1 Topography and Surface Water Hydrology

Langley AFB is located in the coastal plain of southeastern Virginia (Figure 3.1) on the York-James Peninsula, which is bounded by the York River on the northeast, Chesapeake Bay on the east, and the James River on the south and southwest. The area is characterized by a low, flat terrain with no hilly areas nearby. Land surface elevations at Langley AFB are relatively flat and range from 0 to 12 feet above mean sea level (msl).

Generally, the topography in the area surrounding IRP Site SS-16 slopes gently to the southeast toward the Southwest Branch of the Back River. IRP Site SS-16 is relatively flat with elevations ranging from approximately 6 to 8 feet above msl. The streets surrounding the site are slightly lower in elevation to allow for adequate drainage. The parking lot between Buildings 590 and 596 dips slightly to the northeast towards Thompson Street. The grassy area surrounding Building 596 also dips slightly to the northeast. On the northeast side of Thompson Street (opposite the site), the adjacent paved areas dip slightly to the southwest toward Thompson Street.

Langley AFB is located on a wide peninsula where the Southwest and Northwest Branches of Back River join to form the Back River. Both branches of the Back River originate in nearby Newport News City (to the west). From Langley AFB, the Back River flows 3 miles eastward and discharges into Chesapeake Bay (Figure 1.1). The Southwest Branch and Northwest Branch of Back River both experience tidal fluctuations. Normal tidal fluctuations in the area are about 2.5 feet in magnitude (Johnson, 1976). Surface water drainage from Langley AFB flows into Tabbs Creek, Tide Mill Creek, Southwest Branch of Back River, and Northwest Branch of Back River by direct runoff, runoff into artificial and natural drainage features that eventually discharge to these water bodies, and through the Base stormwater drainage system.

IRP Site SS-16 is located in a highly-developed area of the Base, where surface water that does not percolate into the ground flows overland to the Base storm sewer network. Surface water from the parking lot between Buildings 590 and 596 flows to the northeast to storm sewer catch basins located along Thompson Street. These catch basins are connected to a storm sewer that discharges into the Southwest Branch of the Back River near Building 566 at the southeastern terminus of Thompson Street. The Southwest Branch of the Back River is approximately 350 feet southeast of IRP Site SS-16.

3.1.2 Man-made Features

As shown on Figure 2.2, much of the site is asphalt paved (4 to 8 inches in thickness) or covered with buildings. Other areas around the perimeter of the site are covered by manicured grass and shrubs. The majority of precipitation falling on unpaved areas probably infiltrates into the subsurface due to the flat surface topography and permeable, sandy soils. Various underground utilities traverse the site and surrounding areas, including water main, storm sewer, sanitary sewer, electrical, fiber optic (communications), and television cable lines. The majority of these underground utilities

are likely installed above the water table with exception of the storm sewer. A storm sewer identified during the investigation is situated parallel to Thompson Street, adjacent to monitoring points 16MP-6, 16MP-7, and 16MP-8. The elevation of the sewer bottom was measured at approximately 0.2 foot msl, which is below the water table. Stormwaters flow through the sewer in a southeasterly direction and discharge into the Southwest Branch of the Back River. The sandy, highly permeable soils in the saturated zone tend to minimize preferential migration of contaminants along the storm sewer corridor or other utility corridors.

One UST, located immediately southeast of Building 590 (Figure 2.2), was identified during the July 1995 field effort. The tank capacity was 1,000 gallons and was used to store heating oil for Building 590. The UST was found to contain water during the 1995 field investigation.

3.2 REGIONAL GEOLOGY AND HYDROGEOLOGY

Langley AFB is located on the far eastern end of the York-James Peninsula in southeastern Virginia. Known as the Outer Coastal Plain, this area is characterized by a series of plains, created under subaqueous conditions, and scarps, former shorelines of Chesapeake Bay or the James River during the Pleistocene Epoch (Johnson, 1976). Langley AFB lies on the Hampton Flat, which is the principal physiographic feature of lower York County. The Peninsula is bounded on the southwest by the James River and on the east by Chesapeake Bay. Exposed sediments of this area are of Pliocene, Pleistocene, and Holocene (recent) age. Alluvium, marsh sediment, and beach and dune sand also can be found. Surficial soils at Langley AFB consist almost entirely of the Lynnhaven Member of the Tabb Formation, which is described as beach and nearshore marine sand and clay (Johnson, 1976). The Lynnhaven Member ranges in thickness from less than 0.5 foot to 8 feet in the area.

The Coastal Plain of Virginia is characterized by alternating sand and clay deposits that form a series of aquifers and confining units. A surficial aquifer, seven confined aquifers, and intervening confining units are formed by these deposits (Laczniak and Meng, 1988). A list of hydrogeologic units underlying Langley AFB, along with the estimated elevation of the top of each unit and the estimated thickness of each unit, is presented in Table 3.1.

The surficial aquifer at Langley AFB, the Columbia Aquifer, includes Holocene and Pleistocene age sediments and is approximately 50 to 60 feet thick. Sediments of this aquifer include interbedded and intermixed sand, silt, and clay, overlying a gravelly base (Laczniak and Meng, 1988). Groundwater occurs approximately 5 feet bgs (Law, 1991).

Underlying the Columbia Aquifer is the Yorktown Confining Unit, which is approximately 30 feet thick at Langley AFB. This unit consists mainly of silt and clay. Below the Yorktown Confining Unit is the Yorktown-Eastover Aquifer. This aquifer consists of sediments of Pliocene and early Miocene age and is approximately 155 feet thick at the Base. The main component of this aquifer is sand interbedded with silt, clay, shell beds, and gravel. Deposition of these sediments was the result of marine transgression (Laczniak and Meng, 1988).

3.3 SITE GEOLOGY AND HYDROGEOLOGY

3.3.1 Lithology and Stratigraphic Relationships

The subsurface sediments encountered beneath IRP Site SS-16 consist mostly of fine- to very fine-grained sand. Silt was identified in 16MP-10 from 0 to 8 feet bgs and in 16MP-17 from 0 to 6 feet bgs. However, in most borings, silt was encountered only in the top 4 feet of material. Clay layers of 0.5 to 4 feet in thickness were identified in 12 borings. These clay layers are discontinuous and occur with no apparent predictability throughout the site. Trace amounts of shell fragments were found in five shallow borings

TABLE 3.1
HYDROGEOLOGIC UNITS UNDERLYING LANGLEY AFB
IRP SITE SS-16
INTRINSIC REMEDIATION TS
LANGLEY AFB, VIRGINIA

Formation	Estimated Elevation of Top of Unit (ft msl)	Estimated Thickness of Unit (ft)
Columbia Aquifer	+20	60
Yorktown Confining Unit	-40	30
Yorktown-Eastover Aquifer	-70	155
St. Marys Confining Unit	-225	75
Calvert Confining Unit	-300	140
Chickahominy-Piney Point Aquifer	-440	160
Nanjemoy-Marlboro Confining Unit	-600	50
Upper Potomac Confining Unit	-650	70
Upper Potomac Aquifer	-720	120
Middle Potomac Confining Unit	-840	30
Middle Potomac Aquifer	-870	430
Lower Potomac Confining Unit	-1300	60
Lower Potomac Aquifer	-1360	1140
Bedrock	-2500	--

Source: Laczniak and Meng, 1988.

at depths of approximately 2 feet bgs, and in two deep borings (i.e., monitoring points 16MP-21 and 16MP-22) at depths of >12 feet bgs. The deepest boring performed during this investigation was driven to a depth of 24 feet bgs. The shallowest confining unit, the Yorktown Confining Unit, is estimated to occur at 40 feet below msl (Table 3.1).

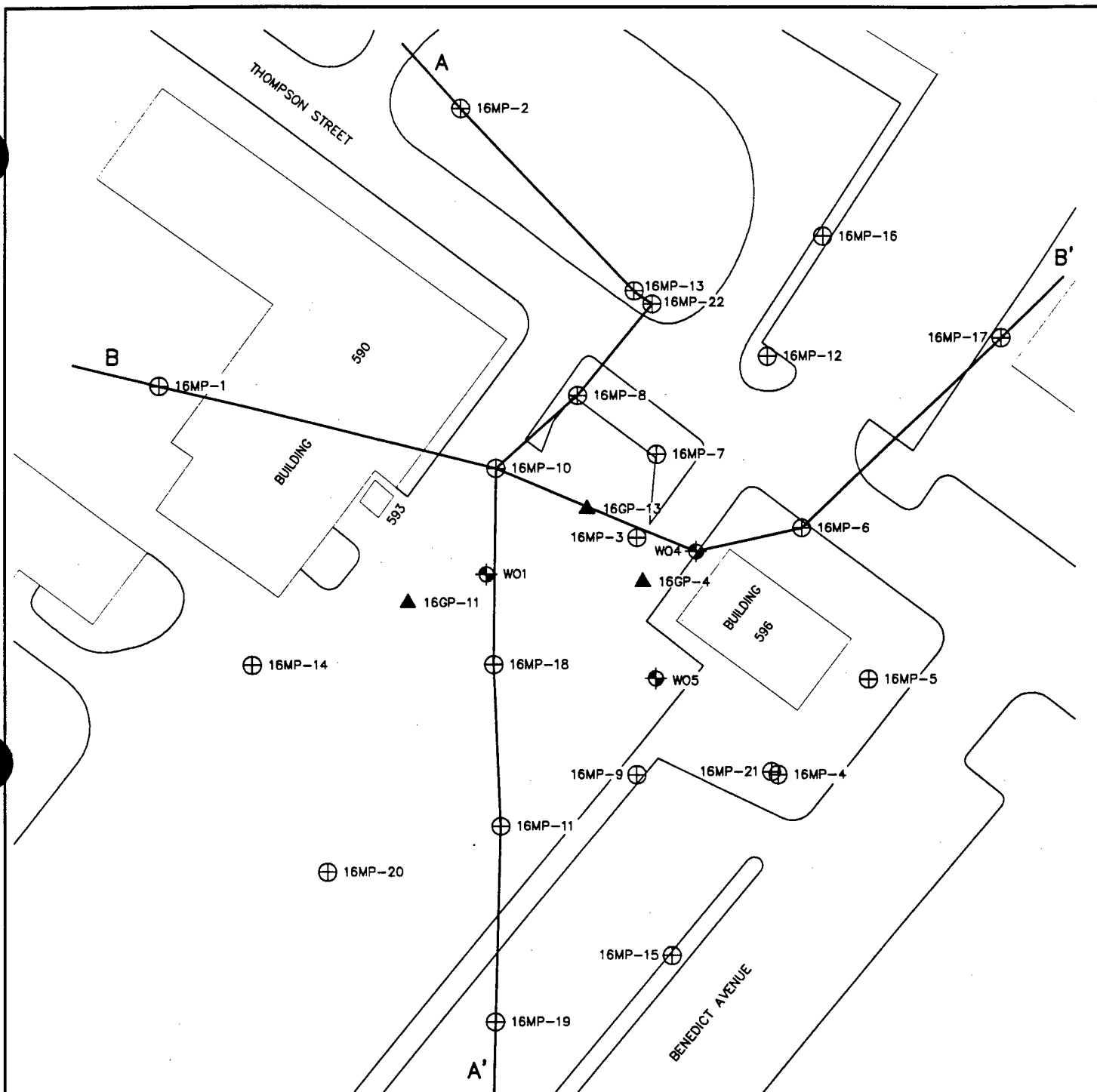
In order to illustrate these stratigraphic relationships, hydrogeologic sections have been developed from subsurface data derived from the July 1995 Geoprobe® investigation. The locations of two site-specific hydrogeologic cross sections are presented on Figure 3.2. Figures 3.3 and 3.4. present hydrogeologic sections A-A' and B-B', which are approximately parallel and perpendicular, respectively, to groundwater flow.

3.3.2 Groundwater Hydraulics

3.3.2.1 Flow Direction and Gradient

The groundwater surface below IRP Site SS-16 was measured during July 1995 at depths from 1.5 to 6.6 feet bgs. The water table was generally encountered at depths greater than 4.5 feet bgs except at monitoring point 16MP-3, in which groundwater was found at a depth of approximately 1.5 feet bgs. Recharge of the shallow groundwater from precipitation is expected to occur in unpaved areas, which occur around the perimeter of the site. A summary of groundwater measurements taken in July 1995 is presented in Table 3.2.

Shallow groundwater flow is controlled by local recharge areas and the Southwest Branch of the Back River. Shallow groundwater at the site and the surrounding areas exhibits a mild radial flow originating from higher water table elevations northeast of the site near 16MP-16 and 16MP-17. A contour map of the water table, as measured on July 19, 1995, is presented on Figure 3.5. Groundwater flow in the source area (between Buildings 590 and 596) varies from west-southwest near 16MP-8 and 16MP-10 to



LEGEND

- WO1  MONITORING WELL
- 16MP-10  MONITORING POINT
- 16GP-11  GEOPROBE BORING
- A—A'  LOCATION OF HYDROGEOLOGIC CROSS-SECTION

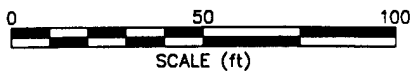
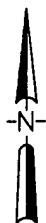


FIGURE 3.2

LOCATION OF HYDROGEOLOGIC CROSS-SECTIONS

IRP SITE SS-16
INTRINSIC REMEDIATION TS
LANGLEY AFB, VIRGINIA



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FIGURE 3.3
HYDROGEOLOGIC CROSS-SECTION A-A'
SITE SS-16
LANGLEY AFB, VIRGINIA

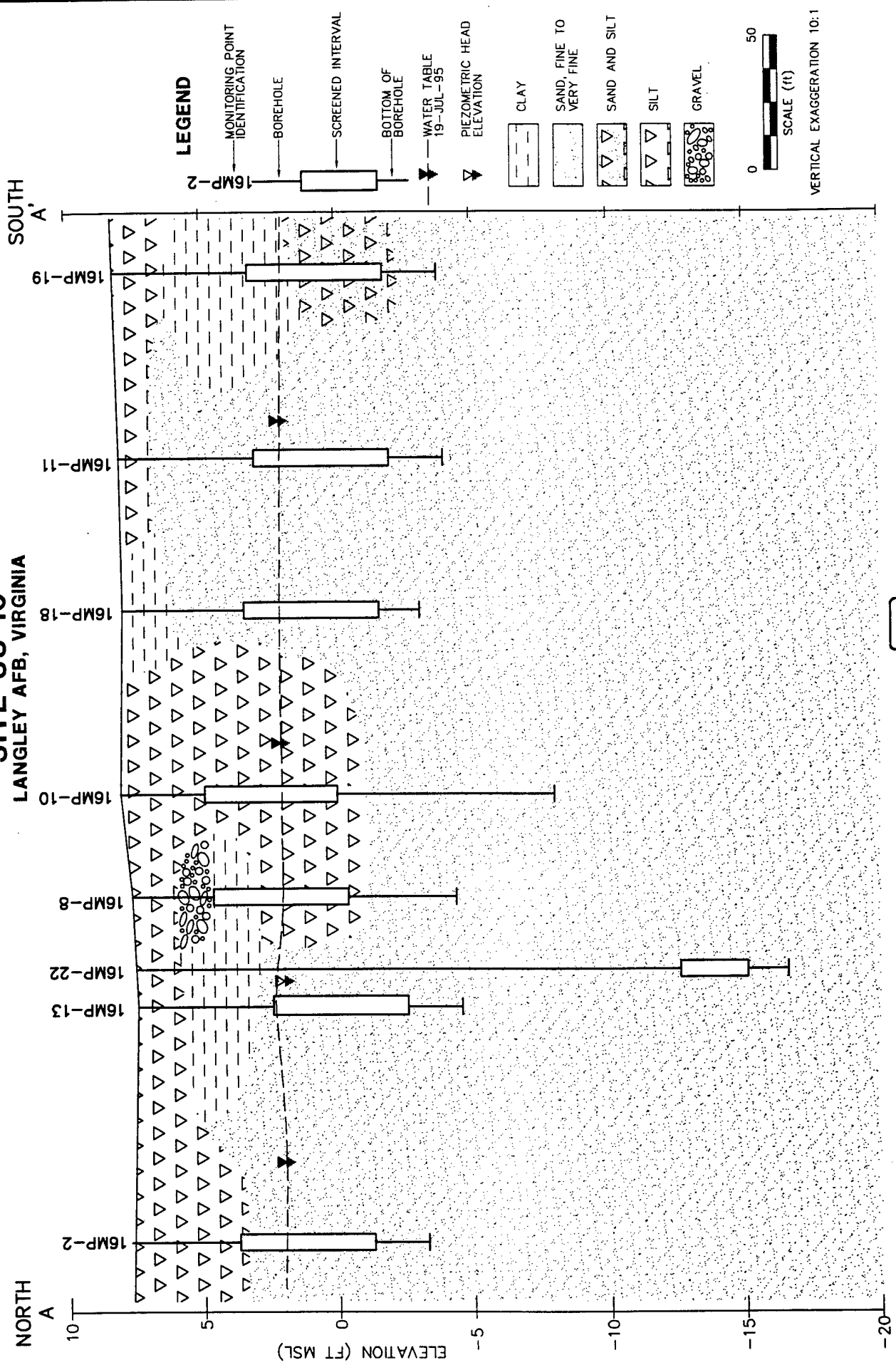
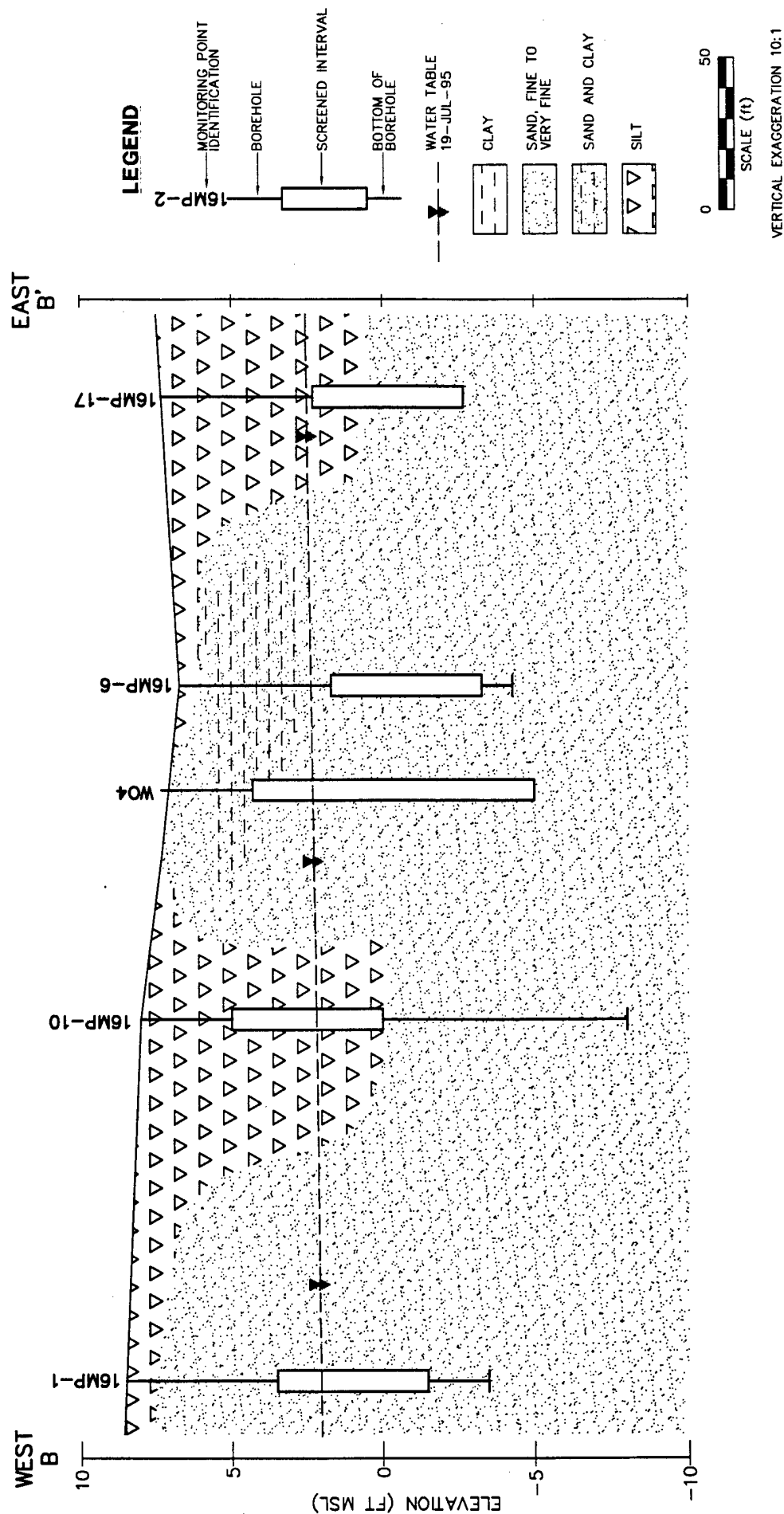


FIGURE 3.4
HYDROGEOLOGIC CROSS-SECTION B-B'
SITE SS-16
LANGLEY AFB, VIRGINIA



SUMMARY OF GROUNDWATER LEVEL MEASUREMENTS

IRP SITE SS-16

INTRINSIC REMEDIATION TS

LANGLEY AIR FORCE BASE, VIRGINIA

Monitoring Point	Northing	Easting	Well Diameter (inches)	Top of Casing Elevation (ft, msl) ^a	Depth to Water 18-JUL-95 (ft, btoc) ^b	Groundwater Elevation (ft, MSL)	Depth to Water 19-JUL-95 (ft, btoc)	Groundwater Elevation (ft, msl)
16MP-1	278456.71	2628420.89	1.0	8.58	6.51	2.07	6.58	2.00
16MP-2	278552.97	2628525.00	0.5	7.90	5.53	2.37	5.61	2.29
16MP-3	278404.46	2628586.04	0.5	7.34	1.45	5.89	1.58	5.76
16MP-4	278322.06	2628635.00	1.0	7.91	5.82	2.09	5.79	2.12
16MP-5	278355.08	2628666.46	1.0	7.91	5.78	2.13	5.73	2.18
16MP-6	278407.98	2628643.18	0.5	6.85	4.36	2.49	4.50	2.35
16MP-7	278433.24	2628592.87	0.5	7.70	5.16	2.54	5.30	2.40
16MP-8	278453.47	2628565.52	1.0	7.79	5.34	2.45	5.52	2.27
16MP-9	278321.94	2628586.00	0.5	8.36	6.17	2.19	6.19	2.17
16MP-10	278428.35	2628537.29	0.5	7.98	5.68	2.30	5.76	2.22
16MP-11	278303.87	2628538.92	1.0	7.90	5.82	2.08	5.85	2.05
16MP-12	278467.16	2628631.34	1.0	7.64	4.99	2.65	5.10	2.54
16MP-13	278489.76	2628584.89	1.0	7.43	4.85	2.58	4.96	2.47
16MP-14	278359.62	2628452.71	1.0	8.09	6.03	2.06	6.03	2.06
16MP-15	278258.65	2628598.13	1.0	7.91	5.91	2.00	5.89	2.02
16MP-16	278508.86	2628650.59	1.0	7.68	4.89	2.79	4.98	2.70
16MP-17	278473.52	2628712.10	1.0	7.47	4.75	2.72	4.78	2.69
16MP-18	278359.95	2628536.40	1.0	7.93	5.76	2.17	5.77	2.16
16MP-19	278235.39	2628537.27	1.0	8.18	7.36	0.82	6.20	1.98
16MP-20	278287.67	2628478.63	1.0	8.20	6.17	2.03	6.19	2.01
16MP-21	278323.10	2628632.73	0.5	7.83	6.03	1.80	5.92	1.91
16MP-22	278489.35	2628585.32	0.5	7.19	4.99	2.20	5.00	2.19
16-W01	278391.49	2628534.07	2.0	7.98	5.78	2.20	5.80	2.18
16-W04	278399.60	2628606.55	2.0	7.17	4.77	2.40	4.91	2.26
16-W05	278355.16	2628592.51	2.0	7.83	5.58	2.25	5.59	2.24

^a ft, msl = Feet above mean sea level.^b ft, btoc = Feet below top of casing.

south-southwest near W04. East of well W04, surrounding Building 596, groundwater flow direction is to the south and southeast toward the Southwest Branch of the Back River.

Hydraulic gradients within the shallow groundwater at the site were estimated at approximately 0.001 foot/foot (ft/ft) to 0.007 ft/ft. The gradients are highest northeast of the source area near Thompson Avenue. The gradients are lowest downgradient of the site to the south and west. The measured groundwater elevations generally decrease to the south and west except at monitoring point 16MP-3, in which the water table elevation was roughly 3 feet higher than surrounding monitoring points and wells. 16MP-3 was installed in the parking lot between Buildings 590 and 596 in an area that had been patched on at least one occasion. Based on available utility maps and the utility location survey completed for the Geoprobe® activities, a 2-inch water service line connects to a 6-inch-diameter water main beneath the asphalt patch. This evidence suggests that this connection has likely been repaired in the past and may be a continuing leak responsible for the elevated water table at 16MP-3.

Comparison of groundwater elevations in nested monitoring points at IRP Site SS-16 (16MP-4/16MP-21 and 16MP-13/16MP-22) indicated that in July 1995, a downward vertical hydraulic gradient was present. Using the head difference between the shallow and deep monitoring points, and the distance between the midpoint of their screens, the magnitude of the downward vertical hydraulic gradient was determined to be 0.013 ft/ft (16MP-4/16MP-21) and 0.020 ft/ft (16MP-13/16MP-22).

3.3.2.2 Hydraulic Conductivity

Parsons ES estimated the horizontal hydraulic conductivity of the surficial aquifer at wells W01, W04, and W05 using rising head slug tests. The test data were analyzed using the method of Bouwer and Rice (1976), as described in Section 2.7. The results of

these slug tests are summarized in Table 3.3. The average site hydraulic conductivity as determined from these tests is 25 feet per day (ft/day). The test data and analyses are included in Appendix B.

3.3.2.3 Effective Porosity

Because of the difficulty involved in accurately determining effective porosity, accepted literature values for the type of soil comparing the shallow saturated zone were used. Walton (1988) gives ranges of effective porosity for fine sand of 0.1 to 0.3. Because the presence of fines tends to decrease the effective porosity, and because lower effective porosities result in higher computed advective groundwater velocities, an effective porosity of 0.2 was assumed for this project.

3.3.2.4 Advective Groundwater Velocity

The advective velocity of groundwater in the direction parallel to groundwater flow is given by:

$$v = \frac{K}{n_e} \frac{dH}{dL}$$

where: v = Average advective groundwater velocity (seepage velocity)

K = Average hydraulic conductivity (25 ft/day)

dH/dL = Average hydraulic gradient (0.004 ft/ft)

n_e = Effective porosity (0.2).

Using this relationship in conjunction with site-specific data, the average advective groundwater velocity at the site in July 1995, was 0.50 ft/day, or approximately 183 feet per year (ft/yr).

3.3.2.5 Tidal Influence Monitoring

Tidal influence monitoring was performed at the Site during the July 1995 field effort to determine if shallow groundwater flow beneath the site was influenced by tidal

TABLE 3.3
SLUG TEST RESULTS
IRP SITE SS-16
INTRINSIC REMEDIATION TS
LANGLEY AFB, VIRGINIA

Monitoring Well	Type of Test	Hydraulic Conductivity (cm/sec)	Hydraulic Conductivity (ft/day)
W01	rising head	0.0085	24
W04	rising head	0.0090	26
W05	rising head	0.0094	27
	Average	0.0090	25

fluctuations in the nearby Back River. Water levels in monitoring wells W01, W04, and W05 and monitoring points 16MP-5, 16MP-8, and 16MP-14 were measured over a period of 24 hours using a Hermit® 2000 Datalogger and pressure transducer system. The collected data are presented graphically in Figures 3.6 and 3.7. Apparent tidal influence was observed in five of the six monitoring locations. In order to confirm that the data is influenced solely by tides, other potential hydrologic mechanisms that could cause water table fluctuations must be identified, and the data must be analyzed to confirm or discount the influence of these mechanisms.

Changes in water table elevation may be caused by a variety of hydrologic phenomena. Hydrologic mechanisms which may cause water table fluctuations include recharge, air entrapment during recharge, evapotranspiration, atmospheric pressure effects, tidal effects, well pumpage, and artificial recharge (e.g., irrigation, leaky ponds, leaky water lines, etc.) (Freeze and Cherry, 1979). The occurrence of each mechanism can be generally characterized as diurnal, seasonal, or long term. Water level data at the Site was collected for a period of 24 hours, thus the mechanisms which may have potentially influenced the water table position would occur on a diurnal or more frequent basis. Freeze and Cherry (1979) identify tidal effects, atmospheric pressure effects, and evapotranspiration as potential diurnal hydrologic mechanisms affecting water table aquifers.

Atmospheric pressure changes may cause water table fluctuations through the movement of water between the capillary fringe and the aquifer. Bouwer (1978) describes the process using the following example. Increases in atmospheric pressure can cause compression of entrapped air in the capillary fringe. As a result, groundwater from the aquifer flows upward into the capillary fringe to occupy the volumetric change in entrapped air, causing a drop in the water table. Daily water table fluctuations of up to 0.2 foot have been observed (Bouwer, 1978). To evaluate the occurrence of this

FIGURE 3.6
TIDAL INFLUENCE MONITORING TEST RESULTS - 16MP-5, 16MP-8, AND W04
IRP SITE SS-16
INTRINSIC REMEDIATION TS
LANGLEY AFB, VIRGINIA

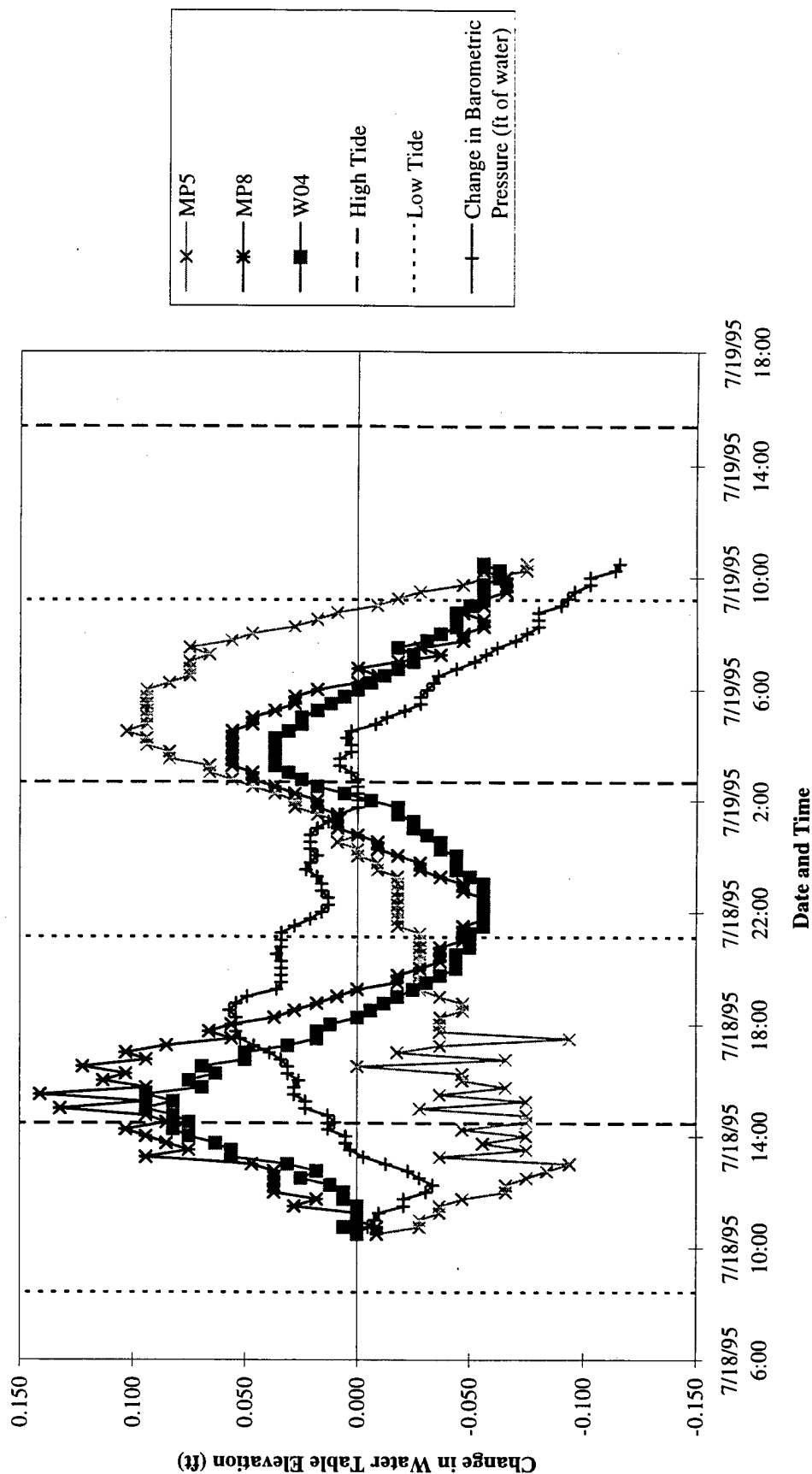
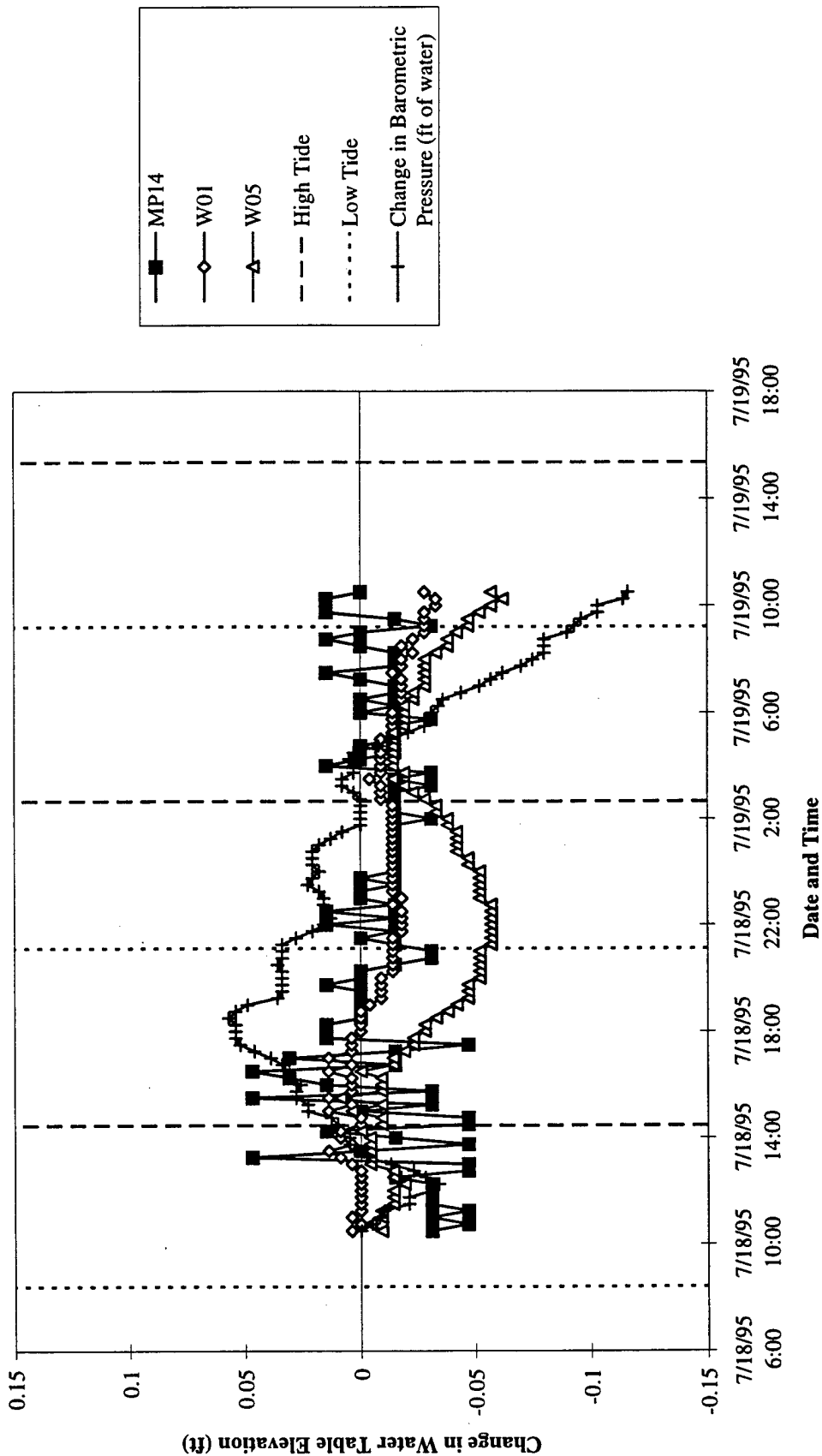


FIGURE 3.7
TIDAL INFLUENCE MONITORING TEST RESULTS - 16MP-14, W01, AND W05
IRP SITE SS-16
INTRINSIC REMEDIATION TS
LANGLEY AFB, VIRGINIA



phenomena, a barometric pressure transducer was used during the monitoring period to measure changes in atmospheric pressure. Visual comparison of the water level data and the barometric pressure data (see Figures 3.6 and 3.7) showed no correlation.

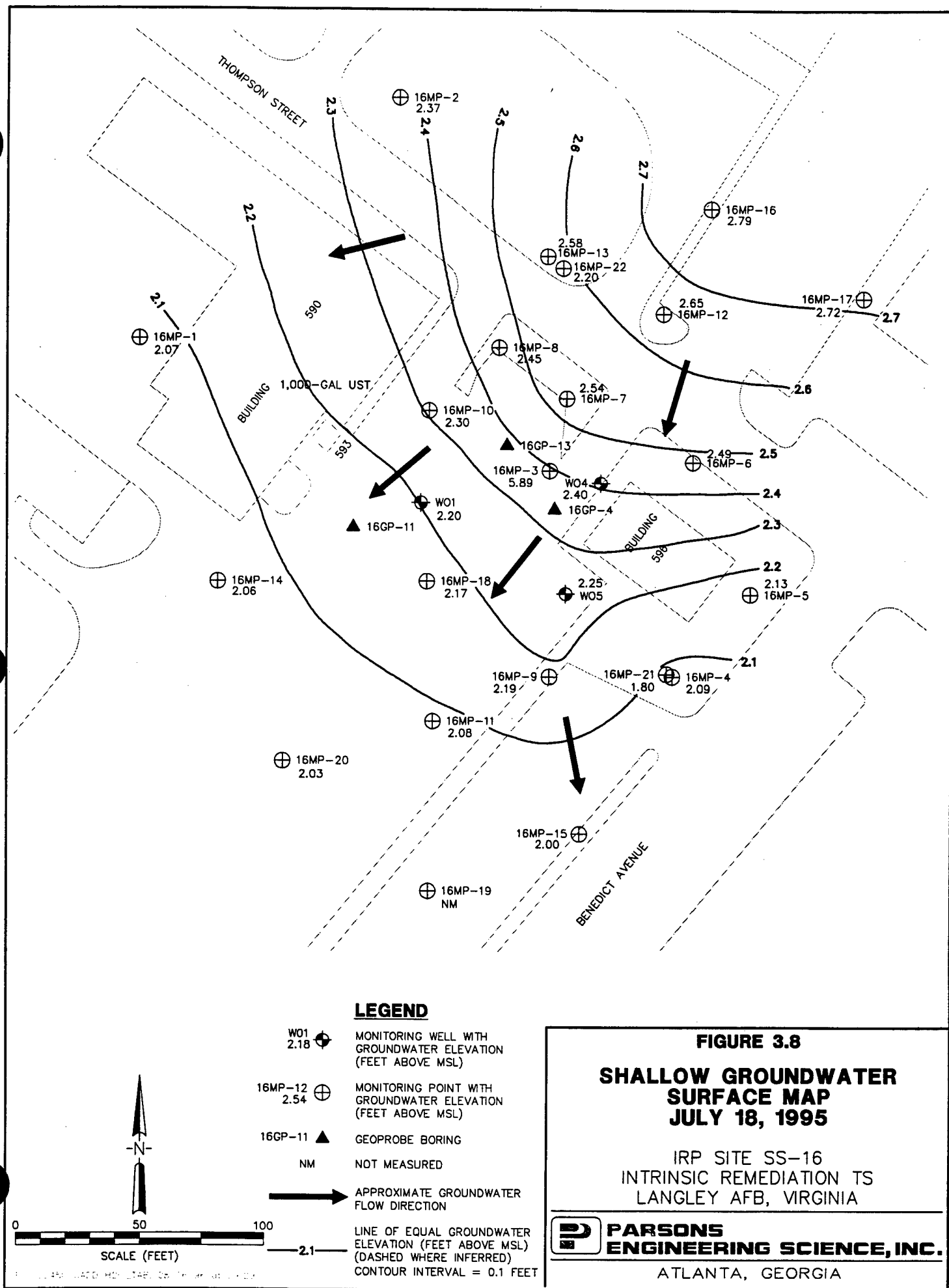
Evapotranspiration is recognized as the combined effect of evaporation and transpiration of soil water which includes moisture in the vadose zone, groundwater in the capillary fringe, and groundwater from the water table aquifer. Evaporation of groundwater is insignificant unless the capillary fringe is close to ground surface (Chow, 1964). Typical capillary fringe heights for fine-grained sands is approximately 2 feet above the water table surface (Bouwer, 1978). The depth to water table across the Site varies from approximately 4.5 to 6.6 feet bgs therefore, the upper surface of the capillary fringe is estimated to be 2.5 feet to 4.6 feet bgs. Evaporation of water from the water table is not considered a significant hydrologic mechanism at IRP Site SS-16 due to the extensive impermeable pavement cover and the depth of the capillary fringe. Transpiration effects (i.e., uptake of groundwater by plant roots) are generally characterized by diurnal water level fluctuations. In areas where the root zone approaches the water table, the water table is lowered via plant root uptake during the daylight hours and recovers during the evening and night when plant root uptake diminishes. The portions of the site not covered by asphalt consist of manicured grass with a few shrubs and trees. In manicured grass areas, the transpiration effects are expected to be minimal. Based on field observations, the root zone for these grasses is estimated to extend less than two feet bgs and do not uptake water from the water table aquifer which occurs at depths of 4.5 to 6.6 feet bgs. Several medium-sized deciduous trees are present between Building 596 and Benedict Avenue in the vicinity of monitoring points 16MP-4, 16MP-5, and 16MP-21. The root systems of these trees extend beneath the water table, and may cause water table fluctuations through transpiration.

Examination of the water level data shows a strong correlation between tidal fluctuations in the Southwest Branch of the Back River and the water table fluctuations observed. The high and low tide times for the Base (Langley AFB, 1995) are shown as vertical dashed and dotted lines on Figures 3.6 and 3.7. The tidal trending was most evident in 16MP-5, 16MP-8, and W04, with minor trending in W01 and W05, and no discernible trending in 16MP-14. The response of the water table lagged behind the tidal changes in the river by approximately 30 minutes to 1 hour.

Groundwater levels in the monitoring points and wells were measured on two occasions (see Table 3.2) corresponding to different stages of tidal response of the water table. The July 19, 1995 measurements (see Figure 3.5) were measured during late falling response (prior to "low tide" response). The measurements from July 18, 1995 were taken during early falling response (during and after "high tide" response). A map of the water table surface as measured on July 18, 1995 is presented in Figure 3.8. Comparison of Figures 3.5 and 3.8 shows that the flow distributions are very similar, with a mild radial flow originating from higher water table elevations northeast of the site near 16MP-16 and 16MP-17. In both cases, groundwater flow in the source area (between Buildings 590 and 596) varies from west-southwest near 16MP-8 and 16MP-10, to south-southwest near W04.

3.3.2.6 Preferential Flow Paths

No preferential flow paths have been identified at the site. Based on groundwater elevations, groundwater flow across the site is mildly radial flowing to the south near Building 596, to the southwest beneath the parking lot located between Buildings 590 and 596, and to the south-southwest beneath Building 590.



3.3.3 Groundwater Use

Drinking water wells were not identified on Langley AFB. The water supply for the Base is obtained from Big Bethel Reservoir. The reservoir is located approximately 1 mile west of the Base.

3.4 CLIMATE

Langley AFB experiences a marine climate characterized by warm, humid, moderately wet summers and mild winters. Average winter temperatures from December through February are 42 degrees Fahrenheit (°F). Spring, summer, and fall mean daily temperatures range from 40°F to 86°F. The mean annual precipitation is 44.5 inches and the mean annual snowfall is 9 inches.

SECTION 4

NATURE AND EXTENT OF CONTAMINATION AND SOIL AND GROUNDWATER GEOCHEMISTRY

4.1 SOURCE OF CONTAMINATION

The suspected sources of contamination at IRP Site SS-16 include several former USTs and ASTs used to store fuel as part of a former service station and a possible former drum storage area (Figure 2.2). The area of concern is paved with asphalt, so there are no indicators of contamination at the surface. A UST was identified during the July 1995 investigation. This UST was located adjacent to Building 590 along the southeast side of the building and had not been identified as a potential source of hydrocarbons during previous investigations. Records pertaining to contents or construction details for the UST could not be located. Subsection 1.2 provides the facility history and more detail regarding the suspected sources of contamination.

4.2 SOIL AND SOURCE CHEMISTRY

4.2.1 Mobile LNAPL Contamination

Mobile light nonaqueous-phase liquid (LNAPL) is defined as the LNAPL that is free to flow in the aquifer and that will flow from the aquifer matrix into a well under the influence of gravity. Mobile LNAPL was not observed in any monitoring wells or monitoring points during the July 1995 field investigation and has not been reported in earlier site investigation records (WAR, 1982; Radian and Law, 1995).

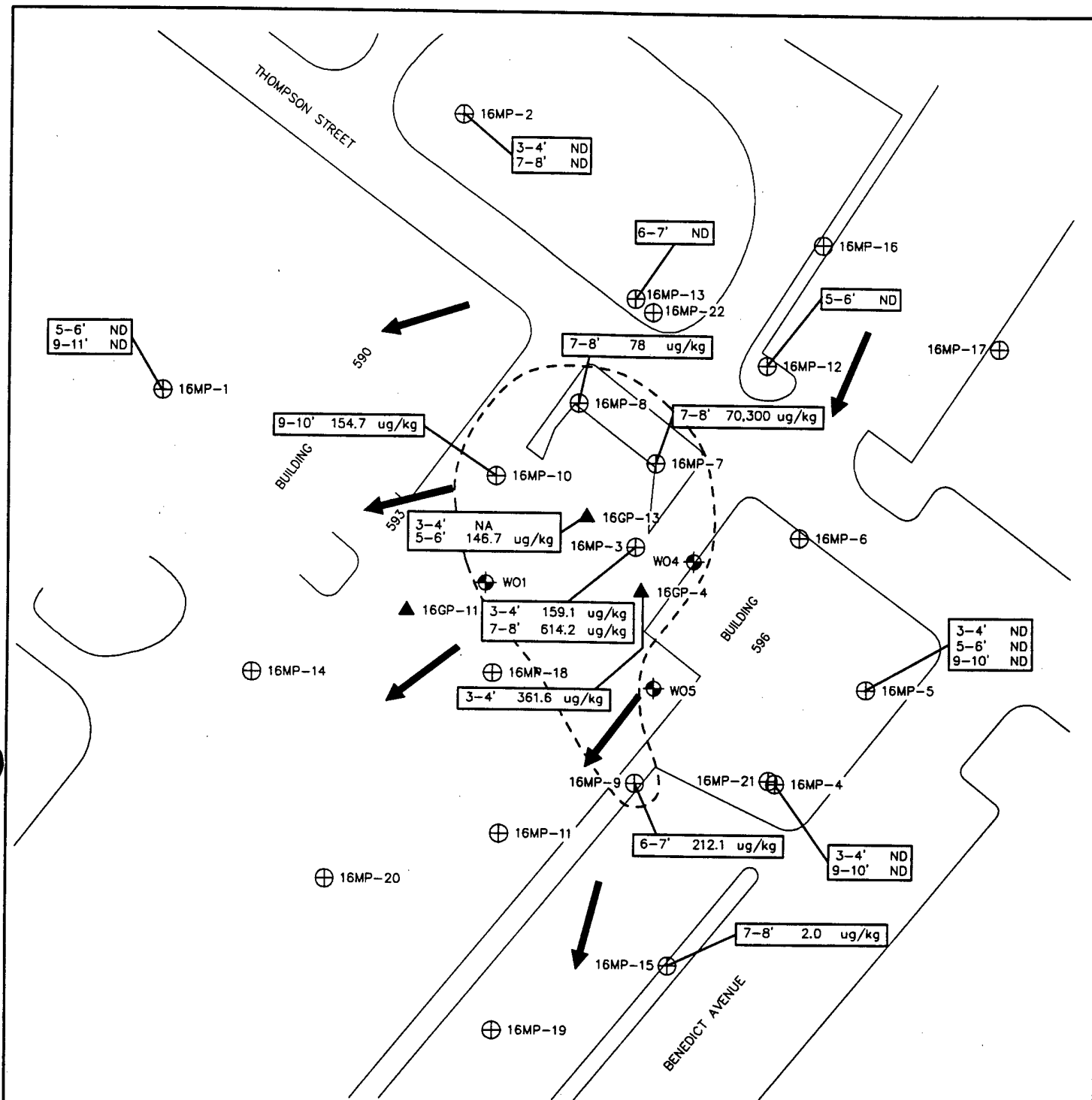
4.2.2 Residual Contamination

Residual LNAPL is defined as the LNAPL that is trapped in the aquifer by the processes of cohesion and capillarity, and therefore will not flow within the aquifer and

will not flow from the aquifer matrix into a well under the influence of gravity. At this site, the residual soil contamination consists of fuel hydrocarbons primarily derived from historic transfer and storage of fuels at the site. The following paragraphs describe the nature and extent of site soil contamination.

Twenty-one soil samples were collected at 14 locations and analyzed for BTEX, total volatile hydrocarbons (TVH), TOC, and arsenic. Detectable levels of BTEX compounds were found in nine of the samples. These detections were also accompanied by the occurrence of strong fuel odors during collection of soil samples from locations 16GP-4, 16GP-13, 16MP-3, 16MP-7, 16MP-8, and 16MP-9. The eight samples collected from these locations are within the estimated extent of residual soil contamination (Figure 4.1). The remaining sample, which was collected from 16MP-15, is located south of the suspected source area. Table 4.1 presents soil sample BTEX results. The highest total BTEX concentration was detected in the soil sample from 7 to 8 feet bgs in 16MP-7 at a concentration of 70,300 micrograms per kilogram ($\mu\text{g/kg}$). The second highest BTEX concentration (614.2 $\mu\text{g/kg}$) was detected in the 7 to 8 feet bgs sample at 16MP-3, located in an area of reported petroleum contamination. The two lowest detected total BTEX concentrations (78 and 2.0 $\mu\text{g/kg}$) were in samples collected from the 7 to 8 feet bgs interval at 16MP-8 and 16MP-15, respectively.

Concentrations of TVH were detected in 8 of 21 soil samples at levels ranging from 1.7 (16MP-10) to 700 (16MP-7) milligrams per kilogram (mg/kg). Analytical results for TVH in soil are presented in Table 4.1. All eight samples also had detections for BTEX. Only the sample with the lowest BTEX concentration (7 to 8 feet bgs from 16MP-15) had a detected BTEX concentration without a detected TVH concentration. The maximum detection of TVH (700E mg/kg) was in the sample (7 to 8 feet bgs from 16MP-7) that also had the highest BTEX concentration.



LEGEND

- W01 MONITORING WELL
- 16MP-10 159.1 MONITORING POINT WITH TOTAL BTEX CONCENTRATION (ug/kg)
- 16GP-11 GEOPROBE BORING
- APPROXIMATE GROUNDWATER FLOW DIRECTION
- ND NOT DETECTED
- NA NOT ANALYZED
- ESTIMATED EXTENT OF RESIDUAL BTEX CONTAMINATION IN SOIL

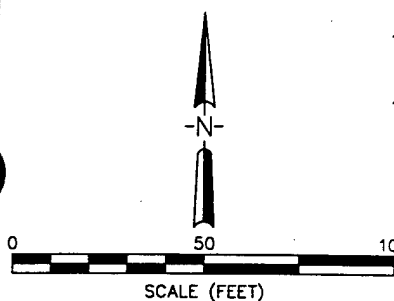


FIGURE 4.1

TOTAL BTEX CONCENTRATIONS IN SOIL JULY 1995

IRP SITE SS-16
INTRINSIC REMEDIATION TS
LANGLEY AFB, VIRGINIA



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TABLE 4.1
1995 SOIL ANALYTICAL RESULTS
SITE SS-16
INTRINSIC REMEDIATION TS
LANGLEY AFB, VIRGINIA

Geoprobe Location	Monitoring Point	Sample Interval (feet bgs)	Benzene (ug/kg)	Toluene (ug/kg)	Ethylbenzene (ug/kg)	Total Xylenes (ug/kg)	Total BTEX ^v (ug/kg)	Chlorobenzene (ug/kg)	1,2,3-TMB ^v (ug/kg)	1,2,4-TMB (ug/kg)	1,3,5-TMB (ug/kg)	1,2,3,4-TEMB ^v (ug/kg)	TVH ^v (mg/kg)	TOC ^v (%)	Arsenic ^v (mg/kg)
16GP-1	16MP-1	5-6	ND ^v	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	NA ^v	9
16GP-1	16MP-1	9-11	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	NA
16GP-2	16MP-2	3-4	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	NA	NA
16GP-2	16MP-2	7-8	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.15	NA
16GP-3	16MP-3	3-4	ND	9.1	20	130	159.1	6.7	59	29	40	550	4.5	NA	12
16GP-3	16MP-3	7-8	3.2 J ^v	29	92	490	614.2	35	1600	410 J	290 B ^v	8800	150	1.86	NA
16GP-4	-	3-4	4.6 J	48	89	220	361.6	24	18 J	50	28 B	160	14	NA	4.7
16GP-5	16MP-4	3-4	ND	ND	ND	ND	ND	ND	0.7 J	ND	2.8 J	2.5 J	ND	NA	NA
16GP-5	16MP-4	9-10	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	NA	NA
16GP-6	16MP-5	3-4	ND	ND	ND	ND	ND	ND	ND	ND	17 J	ND	ND	NA	10.3
16GP-6	16MP-5	5-6	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.07	NA
16GP-6	16MP-5	9-10	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	NA	NA
16GP-8	16MP-7	7-8	ND	5700	8600	56000	70300	3100	5500	5100	5100	14000 B	700 E ^v	NA	NA
16GP-9	16MP-8	7-8	ND	24 J	10 J	44	78	9.0 J	9.8 J	13 J	20 J	20 J	45	0.16	NA
16GP-10	16MP-9	6-7	ND	5.1 J	37	170	212.1	6.5 J	400 J	760	170 J	2700 B	100	NA	NA
16GP-12	16MP-10	9-10	9.7 J	26 J	20 J	99	154.7	11 J	24 J	36	18 J	240	1.7	NA	NA
16GP-13	-	3-4	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	7.6
16GP-13	-	5-6	ND	3.7 J	48	95	146.7	5.9 J	110	240	140	1800	3.3	0.66	NA
16GP-15	16MP-12	5-6	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	NA	NA
16GP-16	16MP-13	6-7	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	NA	NA
16GP-18	16MP-15	7-8	ND	0.9 JB	ND	1.1 JB	2.0	ND	ND	ND	1.4 J	ND	ND	NA	NA

^v BTEX = benzene, toluene, ethylbenzene, and xylenes (USEPA method SW8020).

^v TMB = trimethylbenzene (USEPA method SW8020).

^v TEMB = tetramethylbenzene (USEPA method SW8020).

^v TVH = total volatile hydrocarbons (USEPA method 8015 modified).

^v TOC = total organic carbon (method COU-02).

^v ND = not detected.

^v NA = not analyzed.

^v J = laboratory estimate.

^v B = compound detected in blank.

^v E = laboratory extrapolated value.

TOC concentrations are used to estimate the amount of organic matter sorbed on soil particles or trapped in the interstitial passages of a soil matrix. The TOC concentration in the saturated zone is an important parameter used to estimate the amount of contaminant that could potentially be sorbed to the aquifer matrix. Sorption results in retardation of the contaminant plume relative to the average advective groundwater velocity. A total of 6 soil samples were analyzed for percent TOC. TOC concentrations were detected in five of these samples, and ranged from 0.07 (16GP-6) to 1.86 (16GP-3) percent (Table 4.1).

Arsenic was analyzed for in the suspected source areas because it was detected during a previous investigation at the site (Radian and Law, 1995). Arsenic was analyzed for and detected in five soil samples collected from the vadose zone just above the water table. The detected concentrations ranged from 4.7 to 12 mg/kg (Table 4.1).

4.3 GROUNDWATER CHEMISTRY

Three lines of evidence can be used to document the occurrence of natural attenuation: 1) geochemical evidence; 2) documented loss of contaminant mass at the field scale; and 3) laboratory microcosm studies. Geochemical evidence is used herein as evidence to support the occurrence of natural attenuation at IRP Site SS-16, as described in the following sections. Because this line of evidence strongly suggest that natural attenuation is occurring at this site, laboratory microcosm studies were not deemed necessary. Because both historical site data and the extent of dissolved contamination are limited, the second line of evidence is inconclusive with respect to the occurrences of natural attenuation at this site.

4.3.1 Dissolved Hydrocarbon Contamination

Laboratory analytical results for groundwater samples collected during the Radian and Law (1995) investigation indicated the presence of benzene contamination in the

shallow groundwater beneath the suspected source areas. Benzene was detected in groundwater samples from two of the three monitoring wells sampled at concentrations of 45.7 micrograms per liter ($\mu\text{g/L}$) (W04) and 49.2 $\mu\text{g/L}$ (W05). Groundwater samples collected in July 1995 by Parsons ES personnel confirmed the result from W04. However, benzene was not detected in W05. Table 4.2 summarizes groundwater BTEX results. Trimethylbenzene (TMB) and tetramethylbenzene (TEMB) results are presented in Table 4.3. TMB and TEMB results are presented because they are water-soluble fuel constituents that are considered recalcitrant to biological degradation under anaerobic conditions; therefore, they can be used as tracer compounds in the calculation of anaerobic decay rates for BTEX. Groundwater analytical results from the current investigation are discussed in the following subsections.

4.3.1.1 BTEX in Groundwater

The distribution of total dissolved BTEX in groundwater for July 1995 is presented on Figure 4.2. The extent of the dissolved BTEX plume, as defined by the 10- $\mu\text{g/L}$ contour, contains a total area of approximately 11,300 square feet (0.26 acre), and is estimated to measure approximately 140 feet long along the southwest-northeast axis and roughly 120 feet wide along the southeast-northwest axis. The isolated BTEX detections seen at 16MP-19 are considered anomalous and are not believed to be associated with the main plume. The BTEX concentration of 68 $\mu\text{g/L}$ detected at this location is composed entirely of toluene and is below the current federal maximum contaminant level (MCL) of 1,000 $\mu\text{g/L}$ for toluene (USEPA, 1994). In regards to the BTEX detection seen at 16MP-1, the detection of 20 $\mu\text{g/L}$ detected is composed entirely of toluene (below the current MCL), and is considered anomalous.

Total BTEX was detected at all but one out of 23 monitoring points at concentrations ranging from 0.6 to 123 $\mu\text{g/L}$ (Table 4.2). The maximum BTEX

TABLE 4.2
BTEX, TPH, AND ARSENIC CONCENTRATIONS DETECTED IN 1995 GROUNDWATER SAMPLES
IRP SITE SS-16
INTRINSIC REMEDIATION TS
LANGLEY AFB, VIRGINIA

Sample Location	Sample Date	Benzene ^a (µg/L)	Toluene ^a (µg/L)	Ethylbenzene ^a (µg/L)	Total Xylenes ^a (µg/L)	BTEX ^a (µg/L)	TVH ^a (mg/L)	TEH ^a (mg/L)	Arsenic ^a (mg/L)
16MP-1	13-Jul-95	0.4 U ^a	20	0.4 U	0.4 U	20	0.1U	0.5 U	0.0052
16MP-2	16-Jul-95	0.4 U	3.0 B ^a	0.4 U	0.9 B	3.9	0.1U	NA ^a	NA
16MP-3	16-Jul-95	2.3	19	0.7	1.5	23.5	0.1	NA	0.35
16MP-4	13-Jul-95	0.4 U	1.0	0.4 U	0.4 U	1.0	0.1U	NA	NA
16MP-5	13-Jul-95	0.4 U	3.7	0.4 U	0.4 U	3.7	0.1U	NA	NA
16MP-6	13-Jul-95	0.4 U	9.3	0.4 U	1.4	10.7	0.1U	NA	NA
16MP-7	14-Jul-95	1.3	3.5	1.1	4.4	10.3	0.3	NA	NA
16MP-8	14-Jul-95	0.4 U	15	5.7	27	47.7	4.4	5.1	0.035
MP-8 Duplicate	14-Jul-95	0.4 U	32	16	75	123	11	5.0	0.034
16MP-9	14-Jul-95	0.4 U	7.5	2.4	1.2	11.1	0.1U	NA	NA
16MP-10	16-Jul-95	14	11	2.5	5.5	33	15	4.6	0.097
16MP-11	15-Jul-95	0.4 U	3.3	0.4 U	0.4 U	3.3	0.1U	0.5 U	NA
16MP-12	15-Jul-95	0.4 U	0.6 B	0.4 U	0.4 U	0.6	0.1U	0.5 U	NA
MP-12 Duplicate	15-Jul-95	0.4 U	0.7 B	0.4 U	0.4 U	0.7	0.1U	0.5 U	NA
16MP-13	15-Jul-95	0.4 U	1.2 B	0.4 U	1.5 B	2.7	0.1U	0.5 U	NA
16MP-14	16-Jul-95	0.4 U	5.9	0.4 U	0.4 U	5.9	0.1U	NA	NA
16MP-15	15-Jul-95	0.4 U	2.0 B	0.4 U	0.4 U	2.0	0.1U	NA	NA
16MP-16	15-Jul-95	0.4 U	1.2 B	0.4 U	0.4 U	1.2	0.1U	NA	NA
16MP-17	15-Jul-95	0.4 U	0.9 B	0.4 U	0.4 U	0.9	0.1U	NA	NA
16MP-18	17-Jul-95	0.4 U	3.6	1.6	3.3	8.5	0.3	0.5 U	NA
16MP-19	18-Jul-95	0.4 U	68	0.4 U	0.4 U	68	0.1U	NA	NA
16MP-20	17-Jul-95	0.4 U	2.1	0.4	2.3	4.8	0.1U	NA	NA
W01	13-Jul-95	11	28	4.7	11	54.7	3.4	NA	NA
W04	12-Jul-95	43	6.2	0.4 U	9.8	59	1.4	1.34	0.034
W05	12-Jul-95	0.4 U	0.4 U	0.4 U	0.4 U	<1.6	0.1U	NA	NA

^a By USEPA Method SW8020.

^a TVH = Total volatile hydrocarbons as gasoline (USEPA Method SW8015 modified).

^a TEH = Total extractable hydrocarbons as diesel (USEPA Method SW8015 modified).

^a By USEPA Method SW7060.

^a U = Not detected at the reporting limit.

^a B = Compound detected in blank.

^a NA = Not analyzed.

TABLE 4.3
FUEL TRACER COMPOUNDS DETECTED IN 1995 GROUNDWATER SAMPLES
IRP SITE SS-16
INTRINSIC REMEDIATION TS
LANGLEY AFB, VIRGINIA

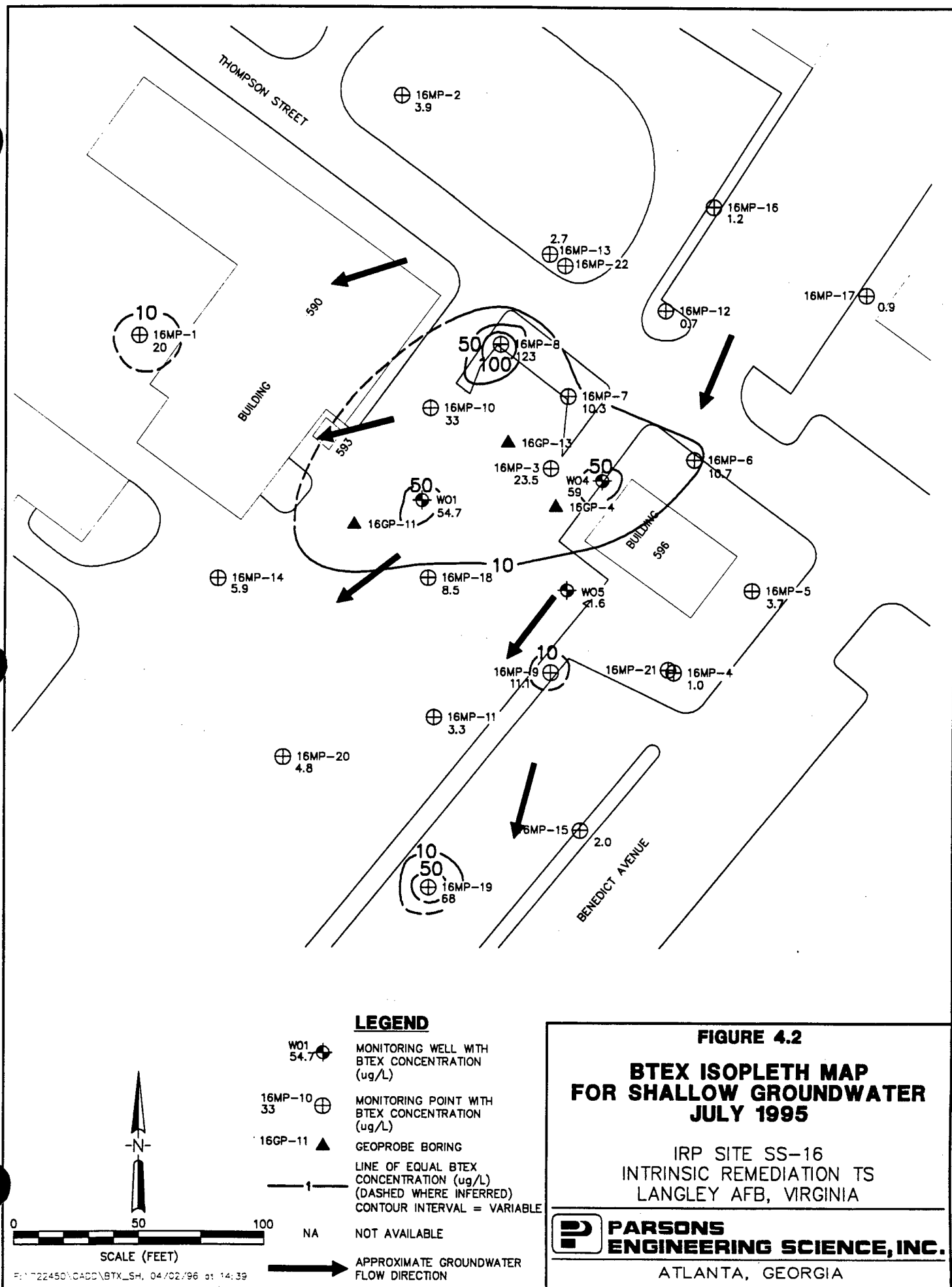
Sample Location	Sample Date	1,2,3-TMB ^u (µg/L)	1,2,4-TMB ^u (µg/L)	1,3,5-TMB ^u (µg/L)	Total TMB ^u (µg/L)	1,2,3,4-TEMB ^u (µg/L)
16MP-1	13-Jul-95	0.6	0.4 U ^u	0.4 U	0.6	0.5 U
16MP-2	16-Jul-95	0.4 U	0.4 U	0.4 U	1.2 U	0.5 U
16MP-3	16-Jul-95	0.7	0.7	0.4 U	1.4	0.5 U
16MP-4	13-Jul-95	1.0	1.2	0.6	2.8	1.1
16MP-5	13-Jul-95	0.9	0.8	0.4 U	1.7	1.0
16MP-6	13-Jul-95	0.6	0.6	0.4 U	1.2	0.6
16MP-7	14-Jul-95	1.1	1.2	2.4	4.7	8.5
16MP-8	14-Jul-95	6.3	8.8	4.8	19.9	45
MP-8 Duplicate	14-Jul-95	15	21	12	48	69 E
16MP-9	14-Jul-95	2.1	17	1.5	20.6	48
16MP-10	16-Jul-95	1.2	2.2	1.0	4.4	57
16MP-11	15-Jul-95	0.4 U	0.4 U	1.0	1.0	0.5 U
16MP-12	15-Jul-95	1.5	0.4 U	0.8	2.3	0.9
MP-12 Duplicate	15-Jul-95	1.1	0.4 U	1.3	2.4	0.5 U
16MP-13	15-Jul-95	0.9	0.9	5.0	6.8	3.8
16MP-14	16-Jul-95	0.4 U	1.0	0.9	1.9	1.4
16MP-15	15-Jul-95	0.9	1.0	1.2	3.1	0.9
16MP-16	15-Jul-95	0.4 U	0.4 U	0.9	0.9	0.5 U
16MP-17	15-Jul-95	0.4 U	0.4 U	1.5	1.5	4.0
16MP-18	17-Jul-95	0.4	0.5	0.4	1.3	2.1
16MP-19	18-Jul-95	0.4 U	0.4 U	0.4 U	1.2 U	0.5 U
16MP-20	17-Jul-95	0.4	0.7	0.4 U	1.1	0.5 U
W01	13-Jul-95	2.9	2.2	4.0 B ^u	5.1	28
W04	12-Jul-95	2.4	0.9	2.7	6.0	33
W05	12-Jul-95	0.4 U	0.4 U	0.4 U	1.2 U	0.5 U

^u TMB = Trimethylbenzene (by USEPA Method SW8020).

^u TEMB = Tetramethylbenzene (by USEPA Method SW8020).

^u U = Not detected at the reporting limit.

^u B = Compound detected in blank.



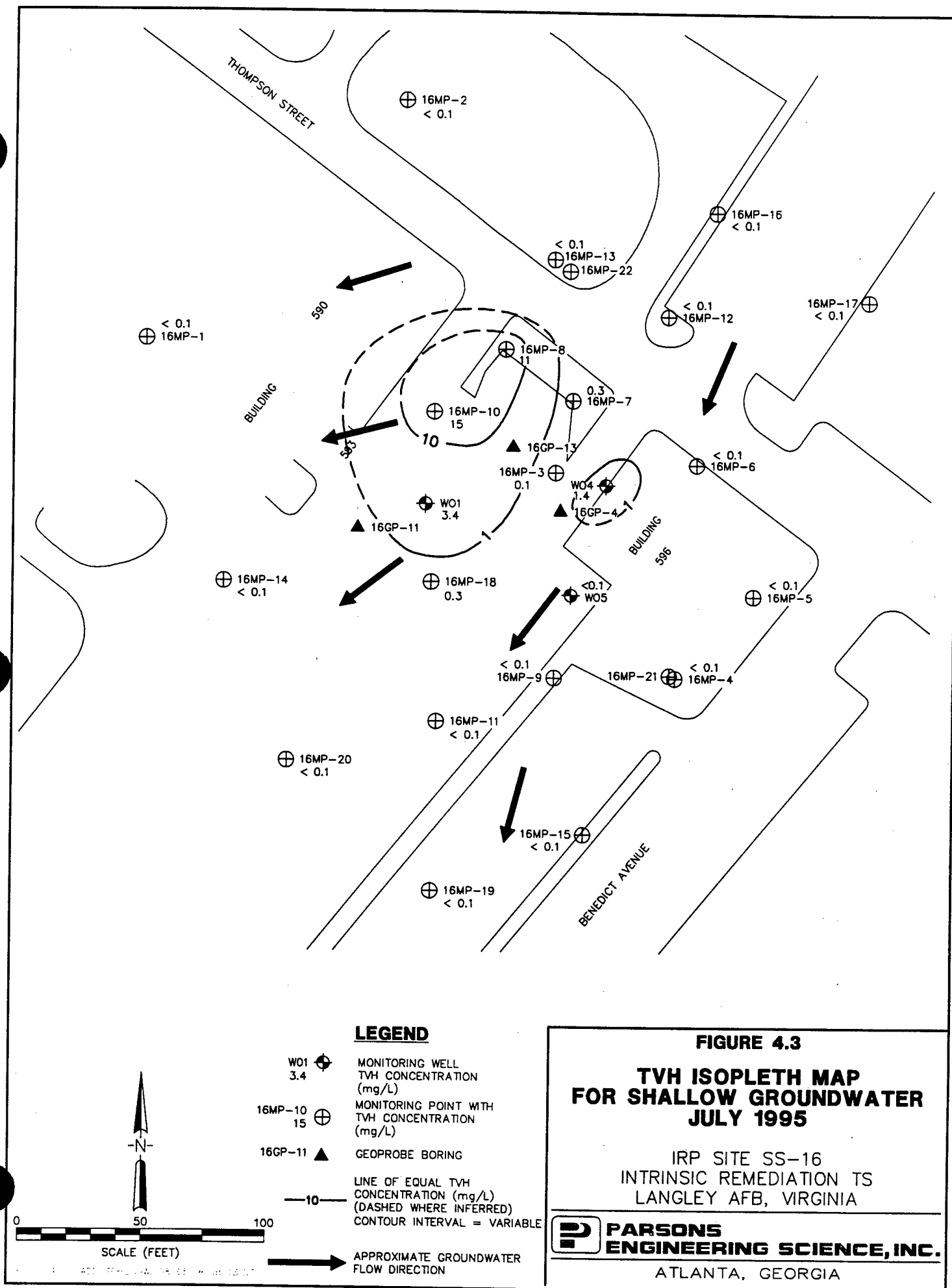
concentration of 123 µg/L was detected in the duplicate sample from 16MP-8 (the primary sample contained 47.7 µg/L BTEX). The maximum benzene concentration of 43 µg/L was detected in the groundwater sample collected from monitoring well W04. Detected benzene concentrations exceeded the federal MCL of 5 µg/L (USEPA, 1994) in groundwater samples collected at 16MP-10, W01, and W04. Toluene concentrations ranged from 0.6 to 68 µg/L, and did not exceed the federal MCL of 1,000 µg/L. The highest concentrations of ethylbenzene (16 µg/L) and total xylenes (75 µg/L) were detected in the duplicate sample from 16MP-8. The federal MCLs for ethylbenzene (700 µg/L) and xylene (10,000 µg/L) were not exceeded in any groundwater sample (USEPA, 1994).

4.3.1.2 TVH and TEH in Groundwater

The distribution of TVH in groundwater, presented on Figure 4.3, is nearly identical to the distribution of BTEX compounds. At no location was TVH detected and BTEX compounds not detected. Detected TVH concentrations ranged from 0.1 to 15 mg/L. TEH (as diesel fuel) was detected in 4 of the 10 samples analyzed (Table 4.2), with detected concentrations ranging from 1.34 to 5.1 mg/L.

4.3.2 Inorganic Chemistry and Geochemical Indicators of BTEX Biodegradation

Microorganisms obtain energy for cell production and maintenance by facilitating thermodynamically advantageous reduction/oxidation reactions involving the transfer of electrons from electron donors to available electron acceptors. This results in the oxidation of the electron donor and the reduction of the electron acceptor. Electron donors at the site are natural organic carbon and fuel hydrocarbon compounds. Fuel hydrocarbons are completely degraded or detoxified if they are utilized as the primary electron donor for microbial metabolism (Bouwer, 1992). Electron acceptors are



elements or compounds that occur in relatively oxidized states, and include oxygen, nitrate, ferric iron, sulfate, and carbon dioxide.

The driving force of BTEX degradation is electron transfer, which is quantified by the Gibbs free energy of the reaction (ΔG°) (Stumm and Morgan, 1981; Bouwer, 1994; Godsey, 1994). The value of ΔG° represents the quantity of free energy consumed or yielded to the system during the reaction. Table 4.4 lists stoichiometry of the redox equations involving BTEX and the resulting ΔG° . Although thermodynamically favorable, most of the reactions involved in BTEX oxidation cannot proceed abiotically because of the lack of activation energy. Microorganisms are capable of providing the necessary activation energy; however, they will facilitate only those redox reactions that have a net yield of energy (i.e. $\Delta G^\circ < 0$). Microorganisms preferentially utilize electron acceptors while metabolizing fuel hydrocarbons (Bouwer, 1992). DO is utilized first as the prime electron acceptor. After the DO is consumed, anaerobic microorganisms use electron acceptors in the following order of preference: nitrate, ferric iron hydroxide, sulfate, and finally carbon dioxide.

Depending on the types and concentrations of electron acceptors present (e.g., nitrate, sulfate, carbon dioxide), pH conditions, and ORP, anaerobic biodegradation can occur by denitrification, ferric iron reduction, sulfate reduction, or methanogenesis (which uses carbon dioxide as the electron acceptor). Other, less common anaerobic degradation mechanisms such as manganese or nitrate reduction may dominate if the physical and chemical conditions in the subsurface favor use of these electron acceptors. Anaerobic destruction of the BTEX compounds is associated with the accumulation of fatty acids, production of methane, solubilization of iron, and reduction of nitrate and sulfate (Cozzarelli *et al.*, 1990; Wilson *et al.*, 1990). Environmental conditions and microbial competition ultimately determine which processes will dominate. Vroblesky

TABLE 4.4
COUPLED OXIDATION REACTIONS FOR BTEX COMPOUNDS
 IRP SITE SS-16
 INTRINSIC REMEDIATION TS
 LANGLEY AIR FORCE BASE, VIRGINIA

Coupled Benzene Oxidation Reactions	ΔG°_r (kcal/mol e Benzene)	ΔG°_r (kJ/mole Benzene)	Stoichiometric Mass Ratio of Electron Acceptor to Compound
$7.5O_2 + C_6H_6 \Rightarrow 6CO_{2g} + 3H_2O$ <i>Benzene oxidation / aerobic respiration</i>	-765.34	-3202	3.07:1
$6NO_3 + 6H^+ + C_6H_6 \Rightarrow 6CO_{2g} + 6H_2O + 3N_{2g}$ <i>Benzene oxidation / denitrification</i>	-775.75	-3245	4.77:1
$3.75 NO_3^- + C_6H_6 + 7.5 H^+ + 0.75 H_2O \Rightarrow 6 CO_2 + 3.75 NH_4^+$ <i>Benzene oxidation / nitrate reduction</i>	-524.1	-2193	2.98:1
$60H^+ + 30Fe(OH)_{3a} + C_6H_6 \Rightarrow 6CO_2 + 30Fe^{2+} + 78H_2O$ <i>Benzene oxidation / iron reduction</i>	-560.10	-2343	21.5:1 ^{a/}
$75H^+ + 3.75SO_4^{2-} + C_6H_6 \Rightarrow 6CO_{2g} + 3.75H_2S^o + 3H_2O$ <i>Benzene oxidation / sulfate reduction</i>	-122.93	-514.3	4.61:1
$4.5H_2O + C_6H_6 \Rightarrow 2.25CO_{2g} + 3.75CH_4$ <i>Benzene oxidation / methanogenesis</i>	-32.40	-135.6	0.77:1 ^{b/}

Coupled Toluene Oxidation Reactions	ΔG°_r (kcal/mole Toluene)	ΔG°_r (kJ/mole Toluene)	Stoichiometric Mass Ratio of Electron Acceptor to Compound
$9O_2 + C_6H_5CH_3 \Rightarrow 7CO_{2g} + 4H_2O$ <i>Toluene oxidation / aerobic respiration</i>	-913.76	-3823	3.13:1
$7.2NO_3 + 7.2H^+ + C_6H_5CH_3 \Rightarrow 7CO_{2g} + 7.6H_2O + 3.6N_{2g}$ <i>Toluene oxidation / denitrification</i>	-926.31	-3875	4.85:1
$72H^+ + 36Fe(OH)_{3a} + C_6H_5CH_3 \Rightarrow 7CO_2 + 36Fe^{2+} + 94H_2O$ <i>Toluene oxidation / iron reduction</i>	-667.21	-2792	21.86:1 ^{a/}
$9H^+ + 4.5SO_4^{2-} + C_6H_5CH_3 \Rightarrow 7CO_{2g} + 4.5H_2S^o + 4H_2O$ <i>Toluene oxidation / sulfate reduction</i>	-142.86	-597.7	4.7:1
$5H_2O + C_6H_5CH_3 \Rightarrow 2.5CO_{2g} + 4.5CH_4$ <i>Toluene oxidation / methanogenesis</i>	-34.08	-142.6	0.78:1 ^{b/}

TABLE 4.4 (CONTINUED)
COUPLED OXIDATION REACTIONS FOR BTEX COMPOUNDS
 IRP SITE SS-16
 INTRINSIC REMEDIATION TS
 LANGLEY AIR FORCE BASE, VIRGINIA

Coupled Ethylbenzene Oxidation reactions	ΔG°_r (kcal/mole Ethyl- benzene)	ΔG°_r (kJ/mole Ethyl- benzene)	Stoichiometric Mass Ratio of Electron Acceptor to Compound
$10.5\text{O}_2 + \text{C}_6\text{H}_5\text{C}_2\text{H}_5 \Rightarrow 8\text{CO}_{2g} + 5\text{H}_2\text{O}$ <i>Ethylbenzene oxidation / aerobic respiration</i>	-1066.13	-4461	3.17:1
$8.4\text{NO}_3 + 8.4\text{H}^+ + \text{C}_6\text{H}_5\text{C}_2\text{H}_5 \Rightarrow 8\text{CO}_{2g} + 9.2\text{H}_2\text{O} + 4.2\text{N}_{2g}$ <i>Ethylbenzene oxidation / denitrification</i>	-1080.76	-4522	4.92:1
$84\text{H}^+ + 42\text{Fe}(\text{OH})_{3a} + \text{C}_6\text{H}_5\text{C}_2\text{H}_5 \Rightarrow 8\text{CO}_2 + 42\text{Fe}^{2+} + 110\text{H}_2\text{O}$ <i>Ethylbenzene oxidation / iron reduction</i>	-778.48	-3257	22:1 ^{a/}
$10.5\text{H}^+ + 5.25\text{SO}_4^{2-} + \text{C}_6\text{H}_5\text{C}_2\text{H}_5 \Rightarrow 8\text{CO}_{2g} + 5.25\text{H}_2\text{S}^0 + 5\text{H}_2\text{O Et}$ <i>Ethylbenzene oxidation / sulfate reduction</i>	-166.75	-697.7	4.75:1
$5.5\text{H}_2\text{O} + \text{C}_6\text{H}_5\text{C}_2\text{H}_5 \Rightarrow 2.75\text{CO}_{2g} + 5.25\text{CH}_4$ <i>Ethylbenzene oxidation / methanogenesis</i>	-39.83	-166.7	0.79:1 ^{b/}

Coupled m-Xylene Oxidation Reactions	ΔG°_r (kcal/mole m-xylene)	ΔG°_r (kJ/mole m-xylene)	Stoichiometric Mass Ratio of Electron Acceptor to Compound
$10.5\text{O}_2 + \text{C}_6\text{H}_4(\text{CH}_3)_2 \Rightarrow 8\text{CO}_{2g} + 5\text{H}_2\text{O}$ <i>m-Xylene oxidation / aerobic respiration</i>	-1063.25	-4448	3.17:1
$8.4\text{NO}_3 + 8.4\text{H}^+ + \text{C}_6\text{H}_4(\text{CH}_3)_2 \Rightarrow 8\text{CO}_{2g} + 9.2\text{H}_2\text{O} + 4.2\text{N}_{2g}$ <i>m-Xylene oxidation / denitrification</i>	-1077.81	-4509	4.92:1
$84\text{H}^+ + 42\text{Fe}(\text{OH})_{3a} + \text{C}_6\text{H}_4(\text{CH}_3)_2 \Rightarrow 8\text{CO}_2 + 42\text{Fe}^{2+} + 110\text{H}_2\text{O}$ <i>m-Xylene oxidation / iron reduction</i>	-775.61	-3245	22:1 ^{a/}
$10.5\text{H}^+ + 5.25\text{SO}_4^{2-} + \text{C}_6\text{H}_4(\text{CH}_3)_2 \Rightarrow 8\text{CO}_{2g} + 5.25\text{H}_2\text{S}^0 + 5\text{H}_2\text{O}$ <i>m-Xylene oxidation / sulfate reduction</i>	-163.87	-685.6	4.75:1
$5.5\text{H}_2\text{O} + \text{C}_6\text{H}_4(\text{CH}_3)_2 \Rightarrow 2.75\text{CO}_{2g} + 5.25\text{CH}_4$ <i>m-Xylene oxidation / methanogenesis</i>	-36.95	-154.6	0.79:1 ^{b/}

^{a/} Mass of ferrous iron produced during microbial respiration.

^{b/} Mass of methane produced during microbial respiration.

and Chapelle (1994) show that the dominant terminal electron accepting process can vary both temporally and spatially in an aquifer with fuel hydrocarbon contamination.

Site SS-16 groundwater data for electron acceptors such as DO, nitrate, and sulfate suggest that intrinsic remediation of hydrocarbons in the shallow aquifer by aerobic respiration, denitrification and sulfate reduction is occurring. In addition, data for ferrous iron (Fe^{2+}) and methane suggest that anaerobic degradation via ferric iron reduction and methanogenesis is occurring. Geochemical parameters for site groundwater are discussed in the following sections.

4.3.2.1 Dissolved Oxygen

DO concentrations were measured at monitoring wells and points at the time of groundwater sampling during July 1995. Concentrations ranged from 0.22 to 6.52 mg/L, with an average shallow groundwater concentration of 2.81 mg/L. The area of lowest DO concentration (<1 mg/L) coincides with the area of highest BTEX concentration. Table 4.5 summarizes measured DO concentrations. A dissolved oxygen isopleth map is presented on Figure 4.4.

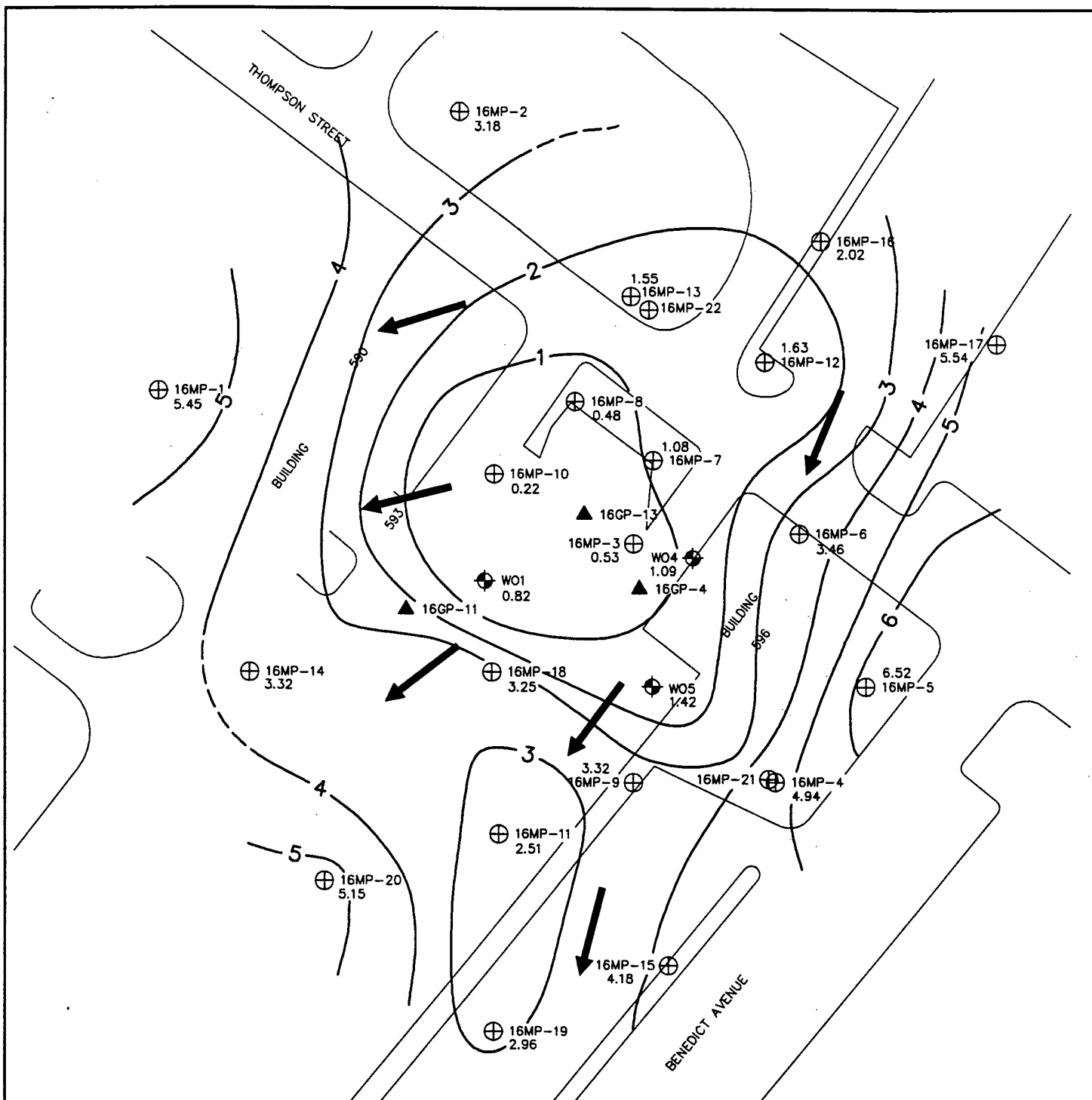
The stoichiometry of BTEX mineralization to carbon dioxide and water caused by aerobic microbial biodegradation is presented in Table 4.4. The average mass ratio of oxygen to total BTEX is approximately 3.14 to 1. This translates to the mineralization of approximately 0.32 mg of BTEX for every 1.0 mg of DO consumed.

As a microbial population in the groundwater grows in response to the introduction of fuel hydrocarbons into the groundwater, some of the fuel is used not only to generate fuel, but also to generate cell mass. When cell mass production is accounted for, the mineralization of benzene to carbon dioxide and water is given by:

TABLE 4.5
GROUNDWATER GEOCHEMICAL DATA
SITE SS-16
INTRINSIC REMEDIATION TS
LANGLEY AFB, VIRGINIA

Sample Location	Sample Date	Dissolved			Ferrous			Total		Carbon Dioxide ^a (mg/L)	Water Temp. ^a (°C) ^a	pH ^a	Ammonia ^a (mg/L)	Chloride ^a (mg/L)
		Oxygen ^a (mg/L)	Nitrate ^a (mg/L)	Nitrite ^a (mg/L)	Iron ^a (mg/L)	Sulfate ^a (mg/L)	Methane ^a (mg/L)	ORP ^a (mV) ^a	Alkalinity ^a (mg/L)					
16MP-1	13-Jul-95	5.45	4.3	<0.076	0.08	30.0	<0.004	204	160	50	23.0	6.3	0.1	24.8
16MP-2	16-Jul-95	3.18	1.7	0.12	0.10	237	0.026	120	240	100	25.9	6.3	0.3	62.0
16MP-3	16-Jul-95	0.53	<0.056	<0.076	3.9	0.72	8.0	-137	280	75	29.2	6.9	15	9.1
16MP-4	13-Jul-95	4.94	1.8	<0.076	0.01	55.3	<0.004	183	240	40	26.1	7.0	0.2	18.9
16MP-5	13-Jul-95	6.52	0.13	<0.076	0.20	60.8	<0.004	199	240	NA ^a	24.0	7.0	NA	12.8
16MP-6	13-Jul-95	3.46	0.76	<0.076	0.07	79.0	<0.004	189	200	20	26.9	7.0	0.1	86.5
16MP-7	14-Jul-95	1.08	<0.056	<0.076	4.9	51.5	NA	-96	280	60	28.2	6.4	2.5	181
16MP-8	14-Jul-95	0.48	0.073	<0.076	7.50	7.4	1.32	-105	280	65	27.1	6.6	2	27.1
16MP-9	14-Jul-95	3.32	0.26	<0.076	3.96	25.2	0.093	-82	280	50	28.8	6.6	2	14.1
16MP-10	16-Jul-95	0.22	<0.056	<0.076	5.50	12.8	1.3	-158	340	70	28.8	6.7	3.5	12.1
16MP-11	15-Jul-95	2.51	0.17	<0.076	6.15	50.8	0.030	-56	240	100	28.3	6.4	2	9.0
16MP-12	15-Jul-95	1.63	<0.056	<0.076	7.25	21.9	0.42	-116	400	100	27.0	6.5	45	71.5
16MP-13	15-Jul-95	1.55	2.3	<0.076	0.12	84.2	0.005	118	200	100	25.5	6.2	0.4	83.6
16MP-14	16-Jul-95	3.32	3.9	<0.076	0.07	25.3	<0.004	102	180	25	29.2	6.8	0.1	25.0
16MP-15	15-Jul-95	4.18	2.9	<0.076	0.24	56.3	<0.004	58	240	70	26.6	6.4	0.2	13.0
16MP-16	15-Jul-95	2.02	5.2	<0.076	0.01	44.7	<0.004	125	240	70	26.7	6.6	3	35.9
16MP-17	15-Jul-95	5.54	1.5	<0.076	0.05	20.3	<0.004	159	160	25	25.2	6.8	0	15.1
16MP-18	17-Jul-95	3.25	0.069	<0.076	3.93	13.1	0.067	-91	240	100	29.8	6.6	2	11.6
16MP-19	18-Jul-95	2.96	4.1	<0.076	0.04	67.2	<0.004	80	340	70	28.5	6.5	0.1	10.7
16MP-20	17-Jul-95	5.15	3.0	<0.076	0.11	23.4	<0.004	24	120	35	28.1	6.6	0.1	303
16-W01	13-Jul-95	0.82	<0.056	<0.076	10.2	<0.25	4.0	NA	480	130	24.3	6.6	6	7.3
16-W04	12-Jul-95	1.09	0.08	<0.076	9.30	2.9	1.71	NA	480	110	23.4	6.9	3	50.6
16-W05	12-Jul-95	1.42	0.11	<0.076	0.39	68.5	<0.004	NA	340	100	23.7	6.6	<1	14.7

^a Field Analysis^a Laboratory analysis.^a ORP = oxidation/reduction potential; mV = Millivolts^a °C = Degrees Celcius.^a NA = Sample not analyzed for this parameter.



LEGEND

WO1 0.82

MONITORING WELL WITH
DISSOLVED OXYGEN
CONCENTRATION (mg/L)

16MP-3 0.53

MONITORING POINT WITH
DISSOLVED OXYGEN
CONCENTRATION (mg/L)

16GP-11

GEOPROBE BORING

— 1 —
LINE OF EQUAL DISSOLVED OXYGEN
CONCENTRATION (mg/L)
(DASHED WHERE INFERRED)
CONTOUR INTERVAL = 1 mg/L

→ APPROXIMATE GROUNDWATER
FLOW DIRECTION

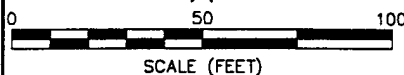
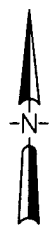


FIGURE 4.4

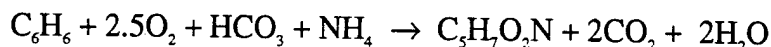
DISSOLVED OXYGEN ISOPLETH MAP FOR SHALLOW GROUNDWATER JULY 1995

IRP SITE SS-16
INTRINSIC REMEDIATION TS
LANGLEY AFB, VIRGINIA



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ATLANTA, GEORGIA



This equation indicates that 5.0 fewer moles of DO are required to mineralize 1 mole of benzene when cell mass production is taken into account. On a mass basis, the ratio of DO to benzene is given by:

$$\text{Benzene} \quad 6(12) + 1(6) = 78 \text{ gm}$$

$$\text{Oxygen} \quad 2.5(32) = 80 \text{ gm}$$

$$\text{Mass Ratio of Oxygen to Benzene} = 80/78 = 1.03:1$$

On the basis of these stoichiometric relationships, 1.03 mg of oxygen are required to mineralize 1 mg of benzene, if cell mass production is taken into account. Similar calculations can be made for toluene, ethylbenzene, and the xylenes. On the basis of these calculations, approximately 0.97 mg of BTEX is mineralized to carbon dioxide and water for every 1.0 mg of DO consumed.

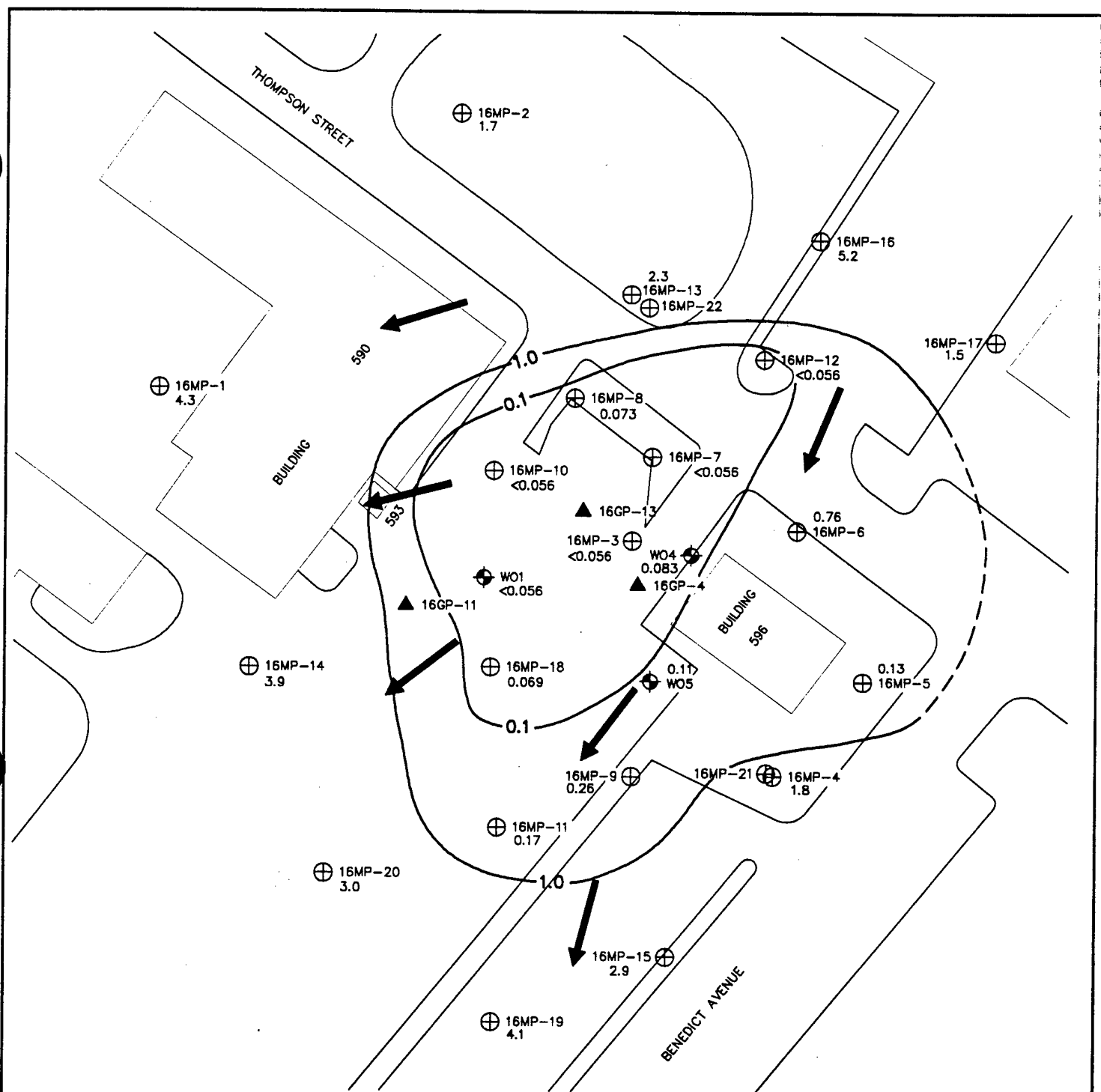
Although this process results in more efficient utilization of electron receptors, it is only applicable as the net cell mass of the microbial population continues to grow. Because groundwater contamination has been present at IRP Site SS-16 for numerous years, it is expected that biomass mass production has reached steady-state. Therefore, the cell mass reaction equations would no longer apply.

A comparison of Figure 4.4 to Figure 4.2 shows that areas of depleted DO correlate well with the highest concentrations of dissolved BTEX. With an average upgradient DO concentration of approximately 3.6 mg/L (16MP-2, 16MP-16, and 16MP-17), the shallow groundwater at this site has the capacity to assimilate 1.1 mg/L (1,100 µg/L) of total BTEX through aerobic biodegradation.

4.3.2.2 Nitrate/Nitrite

Concentrations of nitrate and nitrite were measured in groundwater samples collected in July 1995. Nitrite was detected in only one sample at a concentration of 0.12 mg/L. Nitrate concentrations at the site ranged from <0.056 mg/L to 5.2 mg/L. Table 4.5 summarizes measured nitrate and nitrite concentrations. Figure 4.5 is an isopleth map showing the areal extent of nitrate in groundwater. Comparison of Figures 4.2 and 4.5 shows graphically that the area of depleted nitrate concentrations occupies much of the same area as the dissolved BTEX plume. The nitrate concentration contour of 0.1 mg/L (Figure 4.5) coincides closely to the 10- μ g/L BTEX contour (Figure 4.2). This relationship is a strong indication that anaerobic biodegradation of BTEX compounds is occurring in the shallow groundwater through the microbially mediated process of denitrification.

In the absence of microbial cell production, the stoichiometry of BTEX mineralization to carbon dioxide, water, and nitrogen caused by denitrification is presented in Table 4.4. The average mass ratio of nitrate to total BTEX is approximately 4.9 to 1. This translates to the mineralization of approximately 0.20 mg of BTEX for every 1.0 mg of ionic nitrate consumed. Nitrate concentrations upgradient of the site (16MP-2, 16MP-16, and 16MP-17) ranged from 1.5 mg/L to 5.2 mg/L with an average concentration of 2.8 mg/L. Assuming an average background ionic nitrate concentration of 2.8 mg/L, the shallow groundwater at this site has the capacity to assimilate 0.57 mg/L (570 μ g/L) of total BTEX through denitrification. Because biomass accumulation is not considered, the actual assimilative capacity attributable to sulfate could be somewhat higher.



LEGEND

- W01
 <0.056
 MONITORING WELL WITH
 NITRATE CONCENTRATION
 (mg/L)
- 16MP-3
 <0.056
 MONITORING POINT WITH
 NITRATE CONCENTRATION
 (mg/L)
- 16GP-11
 GEOPROBE BORING
- 0.1
 LINE OF EQUAL NITRATE
 CONCENTRATION (mg/L)
 (DASHED WHERE INFERRED)
 CONTOUR INTERVAL = VARIABLE
- APPROXIMATE GROUNDWATER
 FLOW DIRECTION

FIGURE 4.5

NITRATE ISOPLETH MAP FOR SHALLOW GROUNDWATER JULY 1995

IRP SITE SS-16
INTRINSIC REMEDIATION TS
LANGLEY AFB, VIRGINIA



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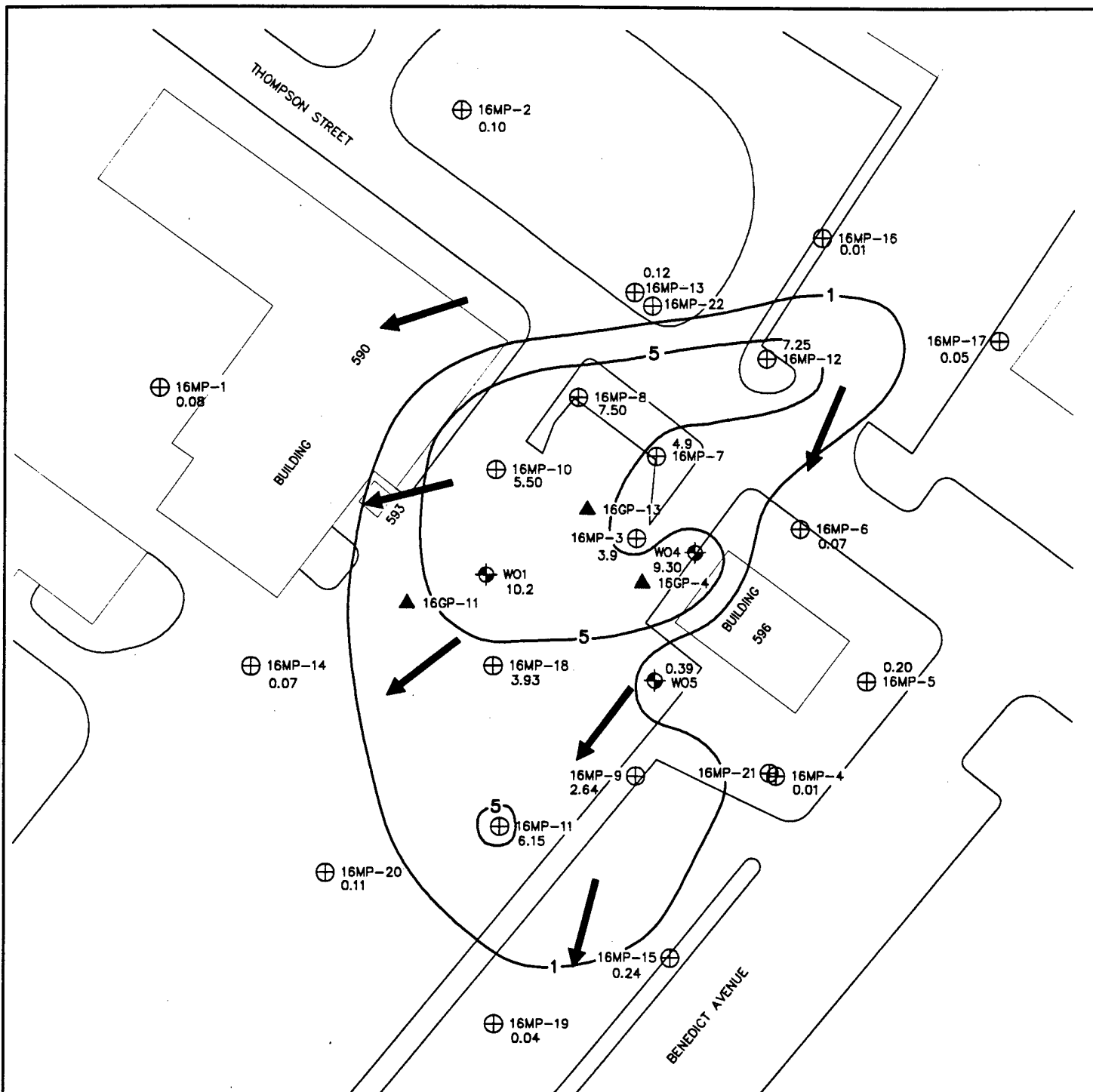
0 50 100
SCALE (FEET)

F:\722450\CADD\NIM_SGW_04/02/96 at 15:10

4.3.2.3 Ferrous Iron

Ferrous iron (Fe^{2+}) concentrations were measured in groundwater samples collected in July 1995. Table 4.5 summarizes ferrous iron concentrations. Measured ferrous iron concentrations ranged from 0.01 mg/L to 9.30 mg/L. Figure 4.6 is an isopleth map showing the areal extent of ferrous iron in groundwater. Comparison of Figures 4.2 and 4.6 shows graphically that most of the area with elevated total BTEX concentrations also has elevated ferrous iron concentrations. This suggests that ferric iron hydroxide (Fe^{3+}) is being reduced to ferrous iron during biodegradation of BTEX compounds. In general, groundwater samples with a ferrous iron concentration greater than 5 mg/L were collected from wells where total BTEX concentrations of at least 10 $\mu\text{g/L}$ were measured. Background concentrations of ferrous iron are generally at or below 0.1 mg/L, as measured at wells with little or no BTEX contamination.

The stoichiometry of BTEX oxidation to carbon dioxide, ferrous iron, and water by iron reduction through anaerobic microbial biodegradation is presented in Table 4.4. On average, 37.5 moles of ferric iron hydroxide are required to metabolize one mole of total BTEX. Conversely, an average of 37.5 moles of ferrous iron are produced for each mole of total BTEX consumed. On a mass basis, this translates to approximately 21.8 mg ferrous iron produced for each 1 mg of total BTEX metabolized. Given a background ferrous iron concentration of approximately 0.1 mg/L and a maximum detected ferrous iron concentration of 9.3 mg/L, the shallow groundwater has the capacity to assimilate approximately 0.42 mg/L (420 $\mu\text{g/L}$) of total BTEX through iron reduction. This is a conservative estimate of the assimilative capacity from iron because this calculation is based on observed ferrous iron concentrations and not on the amount of ferric hydroxide available in the aquifer and solid soil matrix. Therefore, iron assimilative capacity could be much higher.



LEGEND

WO1
10.2

MONITORING WELL WITH
FERROUS IRON CONCENTRATION
(mg/L)

16MP-3
3.9

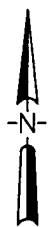
MONITORING POINT WITH
FERROUS IRON CONCENTRATION
(mg/L)

16GP-11

GEOPROBE BORING

LINE OF EQUAL FERROUS IRON
CONCENTRATION (mg/L)
(DASHED WHERE INFERRED)
CONTOUR INTERVAL = VARIABLE

APPROXIMATE GROUNDWATER
FLOW DIRECTION



0 50 100

SCALE (FEET)

FIG 22450\CAD\DWG\SGW, 04/02/96 at 14:47

FIGURE 4.6

FERROUS IRON ISOPLETH MAP FOR SHALLOW GROUNDWATER JULY 1995

IRP SITE SS-16
INTRINSIC REMEDIATION TS
LANGLEY AFB, VIRGINIA



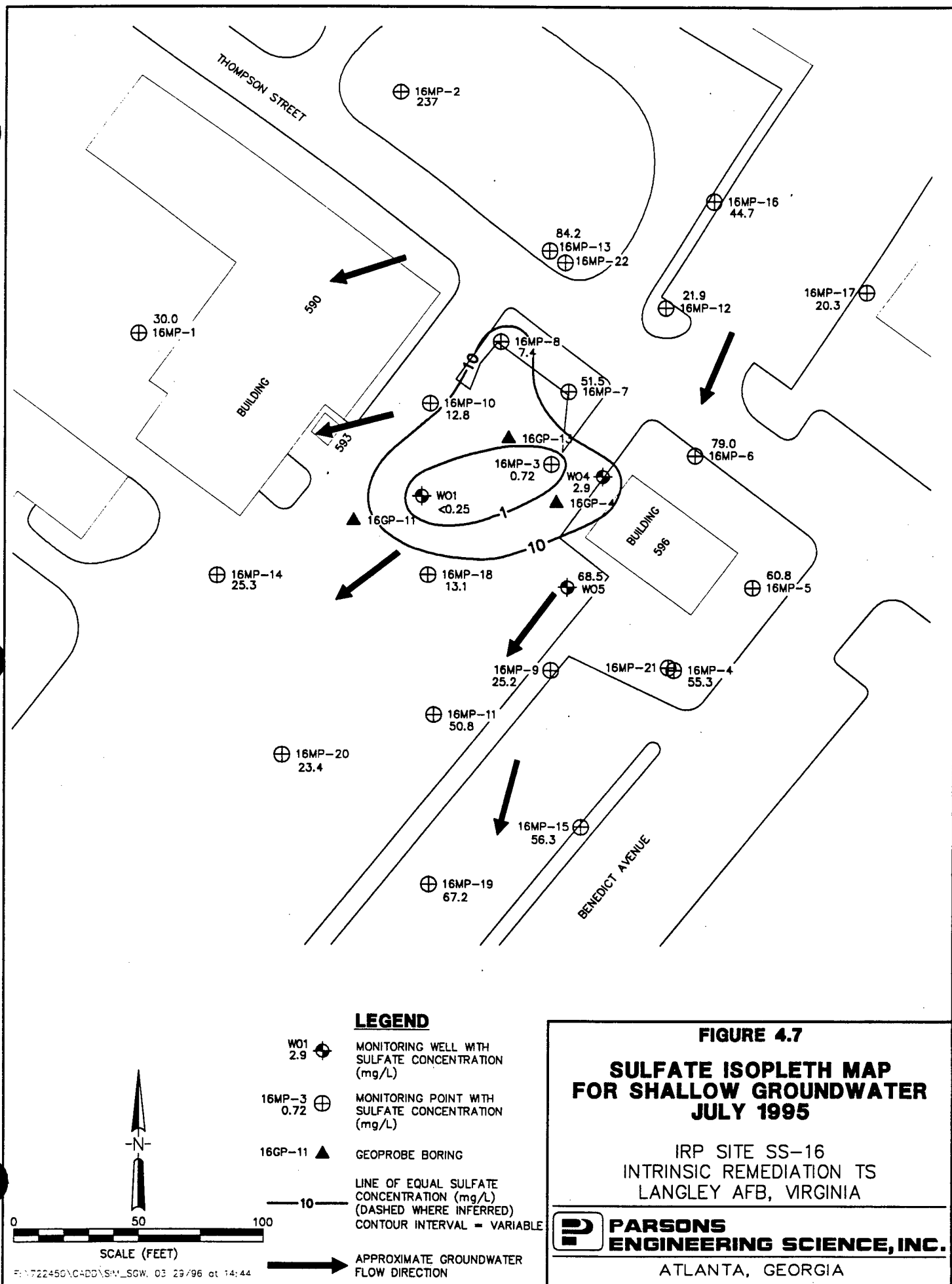
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Recent evidence suggests that the reduction of ferric iron to ferrous iron cannot proceed at all without microbial mediation (Lovley and Phillips, 1988; Lovley *et al.*, 1991; Chapelle, 1993). None of the common organic compounds found in low-temperature, neutral, reducing groundwater could reduce ferric oxyhydroxides to ferrous iron under sterile laboratory conditions (Lovley *et al.*, 1991). This means that the reduction of ferric iron requires microbial mediation by microorganisms with the appropriate enzymatic capabilities. Because the reduction of ferric iron cannot proceed without microbial intervention, the elevated concentrations of ferrous iron that were measured in the contaminated groundwater at the site are a very strong indicator of microbial activity.

4.3.2.4 Sulfate

Sulfate concentrations were measured in groundwater samples collected in July 1995. Sulfate concentrations at the site range from <0.25 mg/L to 237 mg/L. Table 4.5 summarizes measured sulfate concentrations. Sulfate concentrations were less than 85 mg/L in 22 of the 23 groundwater samples collected at the site. Sulfate was detected at a concentration of 237 mg/L in the groundwater sample collected at 16MP-2. This detection is considered anomalous and not representative of typical shallow groundwater at the site. Figure 4.7 is an isopleth map showing the areal extent of sulfate in groundwater. Comparison of Figures 4.2 and 4.7 shows graphically that the area of depleted sulfate concentrations occupies much of the same area as the BTEX plume. Every groundwater sample with a sulfate concentration of less than 10 mg/L had a corresponding total BTEX concentration of at least 20 µg/L (Tables 4.2 and 4.5). This relationship is a strong indication that anaerobic biodegradation of BTEX compounds is occurring in the shallow groundwater through the microbially mediated process of sulfate reduction.

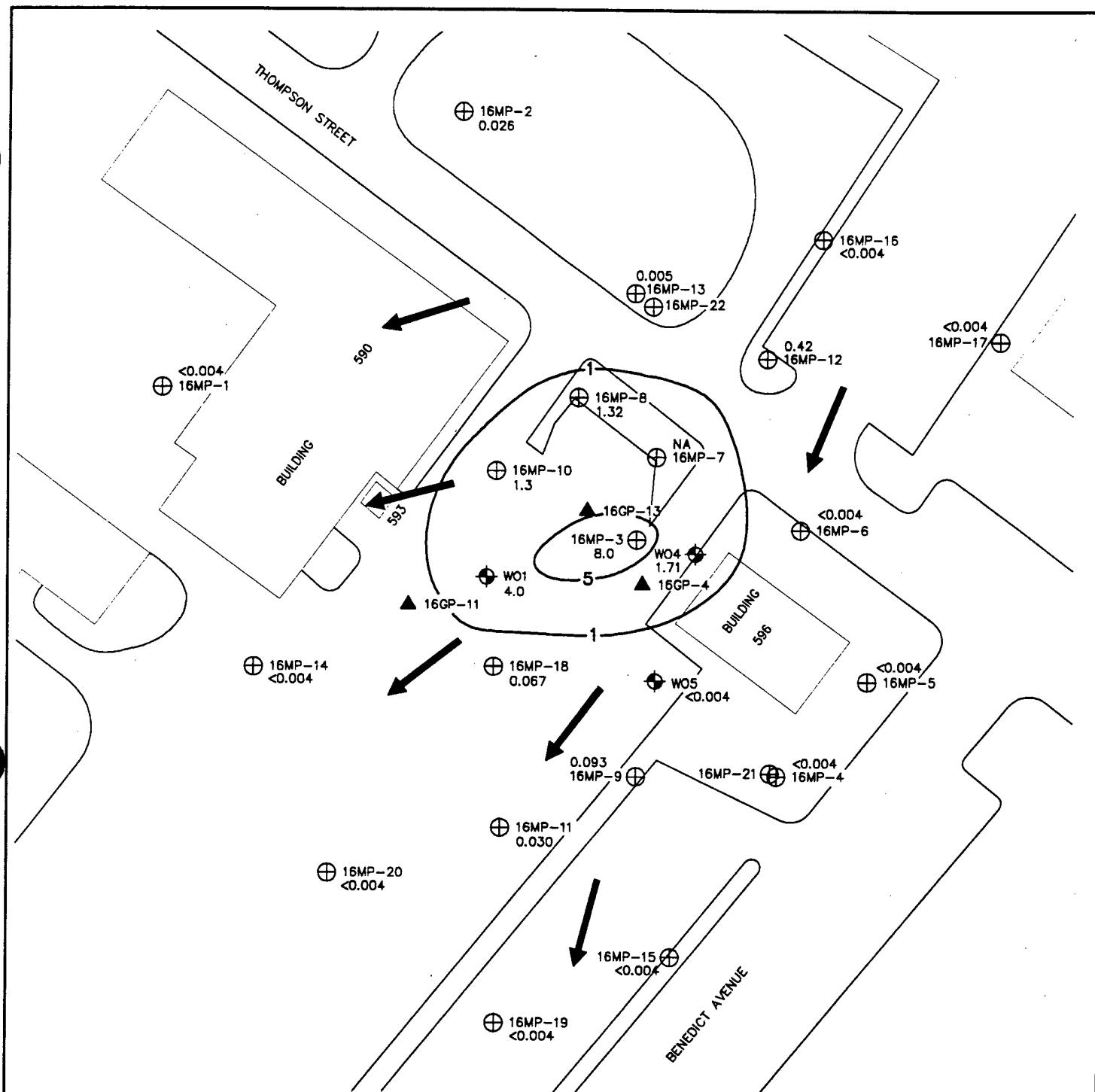


The stoichiometry of BTEX mineralization to carbon dioxide, sulfur, and water by sulfate reduction through anaerobic microbial biodegradation is presented in Table 4.4. The average mass ratio of sulfate to total BTEX is approximately 4.7 to 1. This translates to the mineralization of approximately 0.21 mg of total BTEX for every 1.0 mg of sulfate consumed. Assuming a background sulfate concentration of 32.5 mg/L (average of 16MP-16 and 16MP-17), the shallow groundwater at this site has the capacity to assimilate 6.9 mg/L (6,900 µg/L) of total BTEX through sulfate reduction. Because biomass accumulation is not considered, the actual assimilative capacity attributable to sulfate could be somewhat higher.

4.3.2.5 Methane in Groundwater

Methane concentrations were measured in groundwater samples collected in July 1995. Table 4.5 summarizes methane concentrations which range from <0.004 to 8.0 mg/L at the site. Figure 4.8 is an isopleth map showing the distribution of methane in groundwater. Comparison of Figures 4.2 and 4.8 shows graphically that areas with elevated total BTEX concentrations correlate with elevated methane concentrations. Every groundwater sample with a methane concentration of greater than 1 mg/L had a total BTEX concentration of at least 10 µg/L. This relationship is a strong indication that anaerobic biodegradation of BTEX through methanogenesis is occurring at the site.

The stoichiometry of BTEX oxidation to carbon dioxide and methane by methanogenesis is presented in Table 4.4. On average, approximately 1 mg of total BTEX is degraded for every 0.78 mg of methane produced. Given a maximum detected methane concentration of 8.0 mg/L, the shallow groundwater has the expressed capacity to assimilate approximately 10.3 mg/L (10,300 µg/L) of total BTEX through methanogenesis. This is a conservative estimate of the assimilative capacity through methanogenesis because these calculations are based on observed methane concentrations



LEGEND

WO1 4.0

MONITORING WELL WITH METHANE CONCENTRATION (mg/L)

16MP-3 8.0

MONITORING POINT WITH METHANE CONCENTRATION (mg/L)

16GP-11

GEOPROBE BORING

1

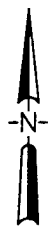
LINE OF EQUAL METHANE CONCENTRATION (mg/L) (DASHED WHERE INFERRED) CONTOUR INTERVAL = VARIABLE

NA

NOT AVAILABLE

→

APPROXIMATE GROUNDWATER FLOW DIRECTION



0 50 100

SCALE (FEET)

FILE: 22450\CADD\MIP_GW, 04/02/96 at 14:52

FIGURE 4.8

METHANE ISOPLETH MAP FOR SHALLOW GROUNDWATER JULY 1995

IRP SITE SS-16
INTRINSIC REMEDIATION TS
LANGLEY AFB, VIRGINIA



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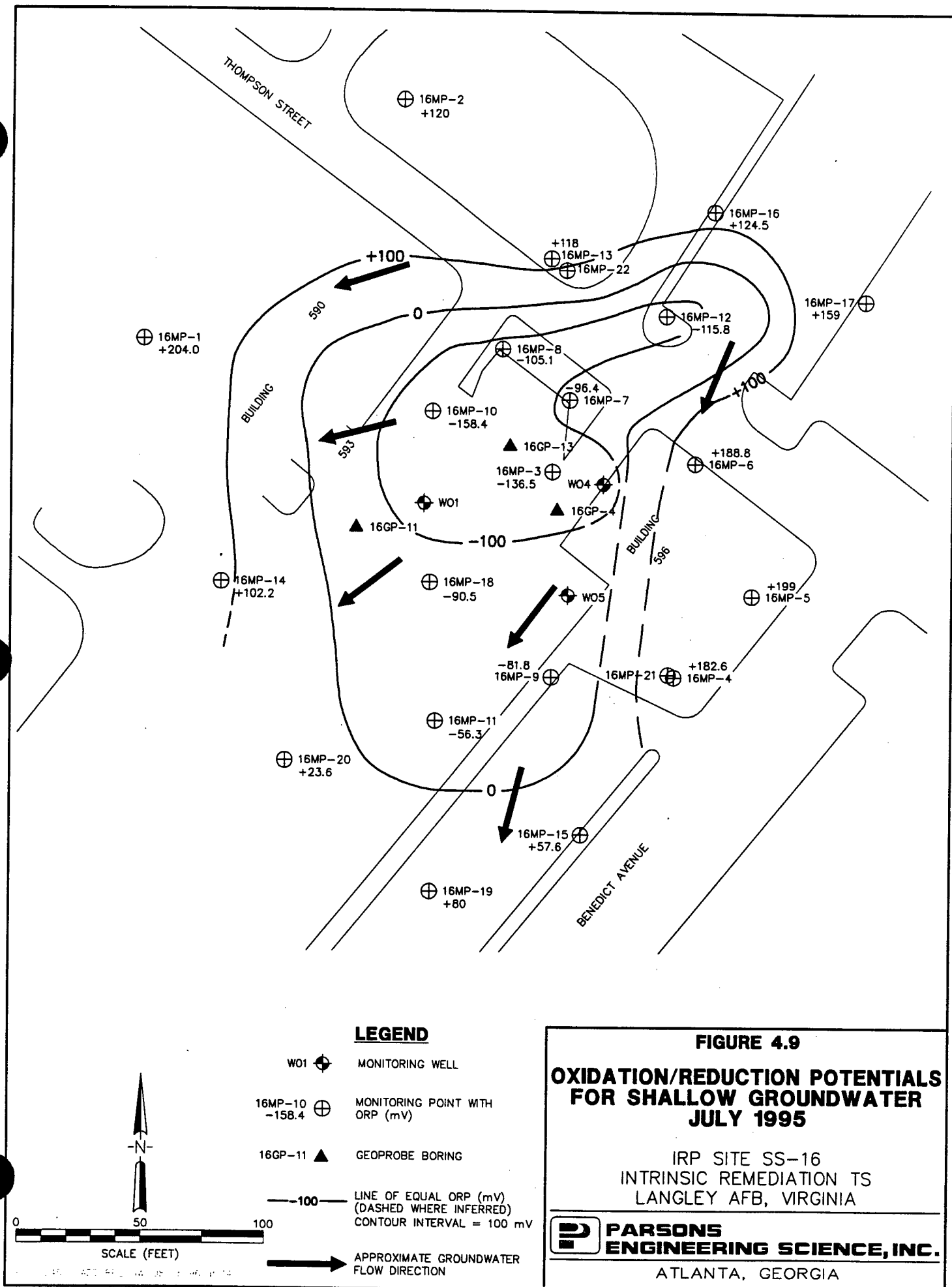
ATLANTA, GEORGIA

and not on the amount of carbon dioxide (the electron acceptor in methanogenesis) available in the aquifer. As methanogenesis produces more carbon dioxide than it consumes, an unlimited supply of carbon dioxide is theoretically available once the process of methanogenesis has been initiated. Therefore, methanogenesis is limited by the rate of reaction rather than the source of electron acceptors.

4.3.2.6 Oxidation/Reduction Potential

ORPs were measured at groundwater monitoring wells and points in July 1995. ORP is a measure of the relative tendency of a solution to accept or transfer electrons. The ORP of a groundwater system depends on which electron acceptors are being reduced by microbes during BTEX oxidation. The ORP at the site ranged from -158.4 millivolts (mV) to 204 mV. Table 4.5 summarizes the ORP data. The areal extent of redox potentials is illustrated graphically on Figure 4.9. As expected, areas at the site with low ORPs appear to coincide with areas of BTEX contamination, low DO, low nitrate, low sulfate concentrations, and elevated ferrous iron and methane concentrations (compare Figure 4.9 with Figures 4.2, 4.4, 4.5, 4.6, 4.7, and 4.8).

ORP is below -100 mV throughout the majority of the site where total BTEX concentrations exceed 10 µg/L; however, this is not as low as predicted from theory for some of the electron acceptor reactions. This discrepancy is a common problem associated with measuring ORP using field instruments. It is likely that the platinum electrode probes are not sensitive to some of the ORP couples (e.g., sulfate/sulfide). Many authors have noted that field-measured redox data alone cannot be used to reliably predict the electron acceptors that may be operating at a site (Stumm and Morgan, 1981; Godsey, 1994; Lovley *et al.*, 1994). Integrating redox measurements with analytical data on reduced and oxidized chemical species allows a more thorough and reasonable interpretation of which electron acceptors are being used to biodegrade site contaminants.



4.3.2.7 Alkalinity

Total alkalinity (as calcium carbonate) was measured in groundwater samples collected in July 1995. These measurements are summarized in Table 4.5. Alkalinity is a measure of the ability of groundwater to buffer changes in pH caused by the addition of biologically generated acids. Total alkalinity at the site is in the moderate range for groundwater, varying from 120 mg/L at well 16MP-20 to 480 mg/L at monitoring wells W01 and W04. This level of alkalinity is sufficient to buffer potential changes in pH caused by biologically mediated BTEX oxidation reactions.

4.3.2.8 pH

pH was measured for groundwater samples collected from groundwater monitoring points and monitoring wells in July 1995. These measurements are summarized in Table 4.5. The pH of a solution is the negative logarithm of the hydrogen ion concentration $[H^+]$. Groundwater pH measured at the site ranges from 6.2 to 7.0 standard units. This range of pH overlaps the optimal range for BTEX-degrading microbes. As with ORP measurements, integrating pH measurements with analytical data on reduced and oxidized chemical species allows a more thorough and reasonable interpretation of whether biodegradation is occurring at the site.

4.3.2.9 Temperature

Groundwater temperature was measured at groundwater monitoring points and monitoring wells in July 1995. Table 4.5 summarizes groundwater temperature readings. Temperature affects the types and growth rates of bacteria that can be supported in the groundwater environment, with higher temperatures generally resulting in higher growth rates. Temperatures in the shallow aquifer varied from 23.0 degrees Celsius ($^{\circ}C$) to 29.8 $^{\circ}C$. These are moderately warm temperatures for shallow groundwater, suggesting that bacterial growth rates should be stimulated.

4.3.3 Discussion

Numerous laboratory and field studies have shown that hydrocarbon-degrading bacteria can participate in the degradation of many of the chemical components of jet fuel and gasoline, including the BTEX compounds (e.g., Jamison *et al.*, 1975; Atlas, 1981, 1984, 1988; Gibson and Subramanian, 1984; Reinhard *et al.*, 1984; Young, 1984; Bartha, 1986; Wilson *et al.*, 1986, 1987, and 1990; Barker *et al.*, 1987; Baedecker *et al.*, 1988; Lee, 1988; Chiang *et al.*, 1989; Grbic-Galic, 1989 and 1990; Cozzarelli *et al.*, 1990; Leahy and Colewell, 1990; Altenschmidt and Fuchs, 1991; Alvarez and Vogel, 1991; Baedecker and Cozzarelli, 1991; Ball *et al.*, 1991; Bauman, 1991; Borden, 1991; Brown *et al.*, 1991; Edwards *et al.*, 1991 and 1992; Evans *et al.*, 1991a and 1991b; Haag *et al.*, 1991; Hutchins and Wilson, 1991; Hutchins *et al.*, 1991a and 1991b; Beller *et al.*, 1992; Bouwer, 1992; Edwards and Grbic-Galic, 1992; Thierrin *et al.*, 1992; Malone *et al.*, 1993; Davis *et al.*, 1994). Biodegradation of fuel hydrocarbons can occur when an indigenous population of hydrocarbon-degrading microorganisms is present in the aquifer and sufficient concentrations of electron acceptors and nutrients, including fuel hydrocarbons, are available to these organisms.

Comparison of BTEX, electron acceptor, and biodegradation byproduct isopleth maps provides strong qualitative evidence for biodegradation of BTEX compounds. Isopleth maps suggest that five electron acceptors are particularly active in the biodegradation of BTEX compounds at the site: DO, nitrate, ferric iron (indicated by the presence of ferrous iron), sulfate, and carbon dioxide (indicated by the presence of methane). The zones of elevated methane concentration, depleted DO concentration, depleted nitrate concentration, depleted sulfate concentration, and elevated ferrous iron concentration coincide with the core region of the BTEX plume.

An interesting indication of aerobic and anaerobic biological activity was observed at monitoring point 16MP-12, which is located upgradient from the suspected source area. Although the detected BTEX concentration at 16MP-12 is low (0.7 µg/L), low ORPs, reduced DO concentrations, depleted nitrate concentrations, and elevated ferrous iron concentrations were detected in the sample collected from 16MP-12. No hydrocarbon constituents were detected in the soil sample from 5 feet to 6 feet bgs) collected at 16MP-12. The evidence of biodegradation at 16MP-12 may be attributable to one or both of the following: seasonal changes in shallow groundwater flow direction (i.e., toward the Southwest Branch of the Back River), or the presence of BTEX and/or TVH in the soil and groundwater beneath Thompson Avenue. The potential for hydrocarbons in the soil and groundwater beneath Thompson Avenue is supported in that the highest concentrations of BTEX and TVH in soil and groundwater were detected at 16MP-7 and 16MP-8 which are located along the opposite side of Thompson Avenue from 16MP-12 (Figures 4.2 and 4.3). Monitoring location 16MP-7 and 16MP-8 are not located near any of the suspected source areas (see Figures 1.4 and 2.2), and the occurrence of hydrocarbons at these locations may be a result of an undocumented spill or remnants of a former mobile LNAPL plume which has since attenuated.

4.3.4 Expressed Assimilative Capacity

The data presented in the preceding sections suggest that mineralization of BTEX compounds is occurring through the microbially mediated processes of aerobic respiration, denitrification, iron reduction, sulfate reduction, and methanogenesis. On the basis of the stoichiometry presented in Table 4.4, the expressed BTEX assimilative capacity for groundwater at the IRP Site SS-16 is at least 19,290 µg/L (Table 4.6). A discussion of the interpretation of expressed assimilative capacity is presented in the following paragraphs.

TABLE 4.6
EXPRESSED ASSIMILATIVE CAPACITY OF SITE GROUNDWATER
 IRP SITE SS-16
 INTRINSIC REMEDIATION TS
 LANGLEY AFB, VIRGINIA

Electron Acceptor or Process	Expressed BTEX Assimilative Capacity ($\mu\text{g/L}$)
Dissolved Oxygen	1,100
Nitrate	570
Iron Reduction	420
Sulfate	6,900
Methanogenesis	10,300
Expressed Assimilative Capacity	19,290

A closed system with 2 liters of water can be used to help visualize the physical meaning of assimilative capacity. Assume that the first liter contains no fuel hydrocarbons, but it contains fuel degrading microorganisms and has an assimilative capacity of exactly "x" μg of fuel hydrocarbons. The second liter has no assimilative capacity; however, it contains fuel hydrocarbons. As long as these 2 liters of water are kept separate, biodegradation of the fuel hydrocarbons will not occur. If these 2 liters are combined in a closed system, biodegradation will commence and continue until the fuel hydrocarbons are depleted, the electron acceptors are depleted, or the environment becomes acutely toxic to the fuel degrading microorganisms. Assuming a non-lethal environment, if fewer than "x" μg of fuel hydrocarbons were in the second liter, all of the fuel hydrocarbons will eventually degrade given a sufficient time; likewise, if greater than "x" μg of fuel hydrocarbons were in the second liter of water, only "x" μg of fuel hydrocarbons would ultimately degrade.

The groundwater beneath a site is an open system, which continually receives additional electron acceptors from through the flow of the aquifer and the percolation of precipitation. This means that the assimilative capacity is not a fixed entity as it is in a

closed system, and therefore cannot be compared directly to contaminant concentration in the groundwater. Rather, the expressed assimilative capacity of groundwater is intended to serve as a qualitative tool. Although the expressed assimilative capacity at this site is greater than the highest measured total BTEX concentration (123 µg/L), the fate of BTEX in groundwater and the potential impact to receptors is dependent on the relationship between the kinetics of biodegradation and the solute transport velocity (Chapelle, 1994). This significant expressed assimilative capacity is a strong indicator that biodegradation is occurring; however, it is not an indication that biodegradation will proceed to completion before potential downgradient receptors are impacted.

At IRP Site SS-16, the groundwater appears to have sufficient assimilative capacity to degrade the observed dissolved BTEX and limit plume migration. BTEX concentrations outside of the identified BTEX core region in soil (see Figure 4.1) and groundwater are below federal MCLs. Natural attenuation of BTEX in groundwater should be considered as the primary component of the remedial solution to be implemented at IRP Site SS-16.

SECTION 5 GROUNDWATER MODEL

5.1 GENERAL OVERVIEW AND MODEL DESCRIPTION

In order to help estimate degradation rates for dissolved BTEX compounds at IRP Site SS-16 and to help predict the future migration of these compounds, Parsons ES modeled the fate and transport of the dissolved BTEX plume. The modeling effort had two primary objectives: 1) to predict the future extent and concentration of the dissolved contaminant plume by modeling the combined effects of advection, dispersion, sorption, and biodegradation; 2) to provide technical support for the evaluation of the intrinsic remediation option at post-modeling regulatory negotiations. The model was developed using site-specific data and conservative assumptions about governing physical and chemical processes. Due to the conservative nature of the model input, the reduction in contaminant mass resulting from the process of natural attenuation is expected to exceed model predictions. This analysis is not intended to represent a baseline assessment of potential risks posed by site contamination.

The Bioplume II code was used to estimate the potential for dissolved BTEX migration and degradation by naturally occurring mechanisms operating at the site. The Bioplume II model incorporates advection, dispersion, sorption, and biodegradation to simulate contaminant plume migration and degradation. The model is based upon the USGS Method of Characteristics (MOC) two-dimensional (2-D) solute transport model of Konikow and Bredehoeft (1978). The model was modified by researchers at Rice University to include a biodegradation component that is activated by a superimposed DO plume. On the basis of the work of Borden and Bedient (1986), the model assumes a reaction between DO and BTEX that is instantaneous relative to the advective

groundwater velocity. Bioplume II solves the USGS 2-D solute transport equation twice, once for hydrocarbon concentrations in the aquifer and once for a DO plume. The two plumes are combined using superposition at every particle move to simulate the instantaneous, biologically-mediated reaction between hydrocarbons and oxygen.

In recent years it has become apparent that anaerobic processes such as denitrification, iron reduction, sulfate reduction, and methanogenesis can be important BTEX degradation mechanisms (Grbic'-Galic', 1990; Beller *et al.*, 1992; Edwards *et al.*, 1992; Edwards and Grbic'-Galic', 1992; Grbic'-Galic' and Vogel, 1987; Lovley *et al.*, 1989; Hutchins, 1991). Because geochemical evidence supports the occurrence of anaerobic biodegradation processes at the site (Section 4.3.2), the combined processes of aerobic and anaerobic biodegradation were considered in modeling BTEX fate and transport at the site. The following subsections discuss in detail the input parameters, the model assumptions, the model calibration, and the simulation results.

5.2 CONCEPTUAL MODEL DESIGN AND ASSUMPTIONS

Prior to developing a groundwater model, it is important to determine if sufficient data are available to provide a reasonable estimate of aquifer conditions. In addition, it is important to ensure that any limiting assumptions can be justified. The most important assumption made when using the Bioplume II model is that oxygen-limited biodegradation is occurring at the site. The Bioplume II model assumes that the limiting factors for biodegradation are: 1) the presence of an indigenous hydrocarbon-degrading microbial population, and 2) sufficient background electron acceptor concentrations. Data and information presented in Sections 3 and 4 suggest that DO, nitrate, ferric hydroxide, sulfate, and carbon dioxide (methanogenesis) are being used as electron acceptors for aerobic and anaerobic biodegradation.

On the basis of the data presented in Section 3, the aquifer is primarily composed of very fine- to fine-grained sand to depths of up to 24 feet bgs. Within these sands, minor amounts of clay, silt, or shell fragments are encountered with no apparent predictability or tendency towards layering. The Yorktown Confining Unit is estimated to occur at 40 feet below msl beneath the site (Lacznia and Meng, 1988) and forms the lower boundary for the water table aquifer. The vertical extent of BTEX in the surficial aquifer is unknown. However, the majority of dissolved BTEX contamination is estimated to preferentially migrate from the site in the uppermost 10 to 15 feet of the aquifer. Groundwater enters the site from saturated soils to the northeast. Site stratigraphy and groundwater elevations suggest that the majority of groundwater at the site flows in a mild radial pattern varying from the west-southwest to southwest within the core region of the BTEX plume (Figure 3.5). A subtler groundwater flow path directs water to the south in the vicinity of 16MP-4, 16MP-5, 16MP-9, and W05; however, this flow path appears to transmit less groundwater than the southwestern flow path.

The water table aquifer was conceptualized and modeled as a shallow unconfined aquifer composed of very fine- to fine-grained sand (Figures 3.3 and 3.4). The average saturated thickness of the aquifer was estimated at 42 feet. The use of a 2-D model is appropriate at IRP Site SS-16 because the shallow saturated zone is relatively homogenous. Furthermore, the local flow system, as defined by the lower Yorktown Confining Unit, inhibits significant downward vertical migration of dissolved BTEX contamination.

BTEX is known to emanate from a fringe of residual soil contamination that resulted from historic fuels storage and possible historic spills during fuel transfer operations. Contaminated soils at the site have not been remediated, although one UST and several ASTs (of unknown content) have been removed. Because the site is no longer used for

fuel storage or transfer, additional fuel releases are not expected at the site. Therefore, only BTEX contamination leaching from the residual LNAPL contamination at the site is considered the only continuing source for the dissolution of BTEX into groundwater over time.

5.3 INITIAL MODEL SETUP

The setup for this model was based on available site data. Where site-specific data were not available (e.g., effective porosity), reasonable assumptions for the types of materials comprising the shallow aquifer were made based on widely accepted literature values. The following sections describe the basic model setup. Those Bioplume II model parameters that were varied during model calibration are discussed in Section 5.4.

5.3.1 Grid Design and Boundary Conditions

The default maximum grid size for the Bioplume II model is limited to 20 columns by 30 rows. The dimension of each column and row can range from 0.1 to 999.9 feet. However, by recompiling the Bioplume II source code with increased row and column limits, a 30- by 40-cell grid was created to model IRP Site SS-16. Each grid cell was 18 feet long by 18 feet wide. The grid was oriented so that the longest dimension was parallel to the dominant southwesterly groundwater flow direction. The grid encompasses the existing BTEX plume with an area of 388,800 square feet, or approximately 9 acres. The full extent of the model grid is indicated on Figure 5.1.

Model boundaries are mathematical statements that represent hydrogeologic boundaries, such as areas of specified head (i.e., surface water bodies or contour lines of constant hydraulic head) or specified flux. Hydrogeologic boundaries are represented by three mathematical statements that describe the hydraulic head at the model boundaries.

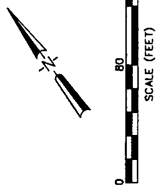
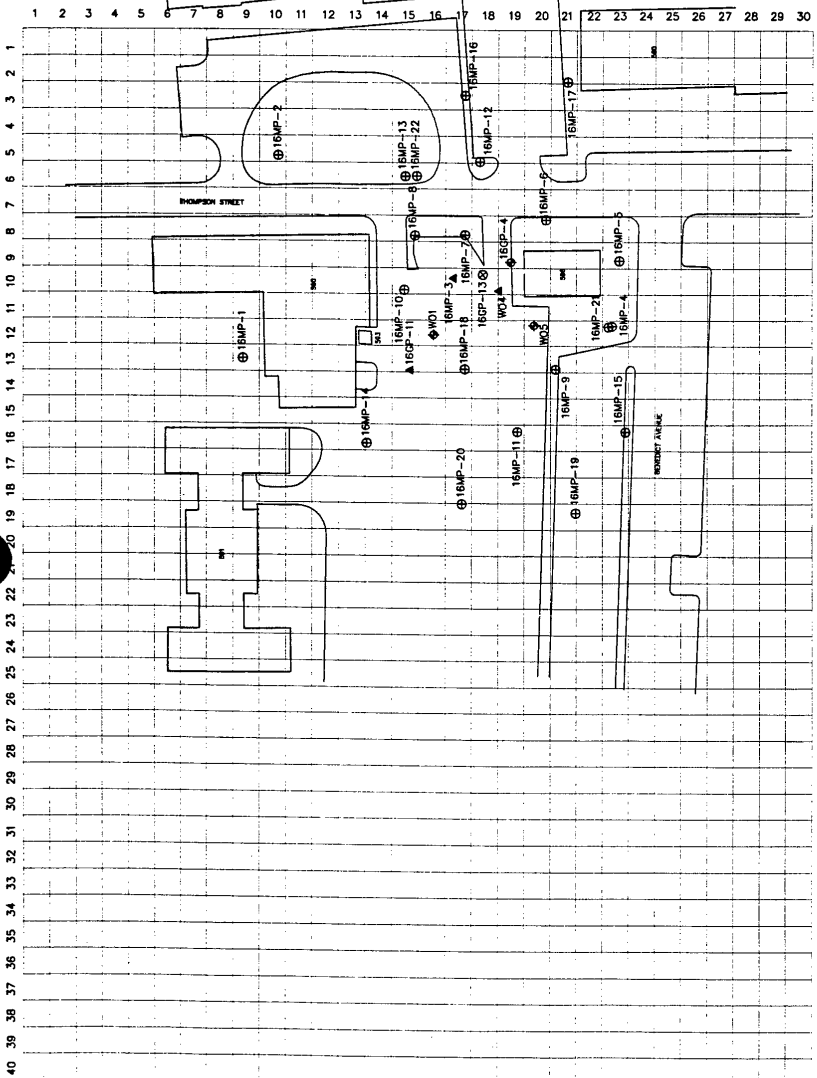


FIGURE 5.1

MODEL GRID

IRP SITE SS-16
INTRINSIC REMEDIATION TS
LANGLEY AFB, VIRGINIA



LEGEND

- WO1 ◆ MONITORING WELL
- 16MP-12 ⊕ MONITORING POINT
- 16GP-11 ▲ GEOPROBE BORING

These include:

- Specified-head boundaries (Dirichlet condition) for which the head is determined as a function of location and time only. Surface water bodies exhibit constant-head conditions. Specified-head boundaries are expressed mathematically as:

$$Head = f(x, y, z, t)$$

where f is the function symbol, x , y , and z are position coordinates, and t is time.

- Specified-flow boundaries (Neumann conditions) for which the mathematical description of the flux across the boundary is given. The flux is defined as a volumetric flow rate per unit area (i.e., ft³/ft²/day). No-flow boundaries are a special type of specified-flow boundary and are set by specifying the flux to be zero. Examples of no-flow boundaries include groundwater divides and impermeable hydrostratigraphic units. Specified-flux boundaries are expressed mathematically as:

$$Flux = f(x, y, z, t)$$

- 3) Head-dependent flow boundaries (Cauchy or mixed-boundary conditions) where the flux across the boundary is calculated from a given boundary head value. This type of flow boundary is sometimes referred to as a mixed-boundary condition because it is a combination of a specified-head boundary and a specified-flow boundary. Head-dependent flow boundaries are used to model leakage across semipermeable boundaries. Head-dependent flow boundaries are expressed mathematically as (Bear, 1979):

$$Flux = \frac{(H_0 - H)K'}{B'}$$

Where: H = Head in the zone being modeled (generally the zone containing the contaminant plume)

H_0 = Head in external zone (separated from plume by semipermeable layer)

K' = Hydraulic conductivity of semipermeable layer

B' = Thickness of semipermeable layer.

Natural hydraulic boundaries are modeled using a combination of the three types of model boundary conditions listed above. When possible, hydrologic boundaries such as surface water bodies, groundwater divides, contour lines, or hydrologic barriers should coincide with the perimeter of the model. In areas lacking obvious hydrologic boundaries, specified-head or specified-flux boundaries can be specified at the model perimeter if the boundaries are far enough removed from the contaminant plume that transport calculations are not affected. Bioplume II requires the entire model domain to be bounded by zero-flux cells (also known as no-flow cells), with other boundary conditions established within the subdomain specified by the no-flow cells.

Specified-head boundaries for the model were set on all sides of the model grid. Typically in two-dimensional models, two rows of specified-head boundaries are sufficient to simulate the flow of groundwater for sites that are hydrogeologically complex or bounded by adjacent lakes or streams. However, placement of specified-head cells on all sides of the model grid for Site SS-16 was appropriate because groundwater flow at the site is slightly radial where groundwater flows in or out of all sides of the model domain. The head of the northeastern boundary was estimated to vary from 2.1 to 2.7 feet above msl and represents the level of groundwater in this portion of the site. The heads of the southeastern and northwestern model boundaries were estimated from 1.6 to 2.6 feet above msl and from 1.5 to 2.1 feet above msl, respectively. The heads along the southwestern model boundary were estimated from 1.5 to 1.6 feet above msl.

The base or lower boundary of the model is assumed to be no-flow, and is defined by the upper surface of the Yorktown Confining Unit located at approximately 40 feet below msl. The upper model boundary is defined by the simulated water table surface.

5.3.2 Groundwater Elevation and Gradient

The water table elevation map presented in Figure 3.5 was used to define the heads used as initial input into the Bioplume II model. Groundwater flow in the vicinity of the Site SS-16 varies in a radial pattern from the west-southwest to the south, with a gradient range over the modeled area of approximately 0.007 ft/ft to 0.001 ft/ft. Gradients are lowest downgradient from the site in the vicinity of monitoring locations 16MP-11, 16MP-14, and 16MP-20 and upgradient in the vicinity of Thompson Street. The water table aquifer at the site is tidally-influenced; however, significant changes in hydraulic gradient and groundwater flow direction do not occur as a result (Section 3.3.2.5).

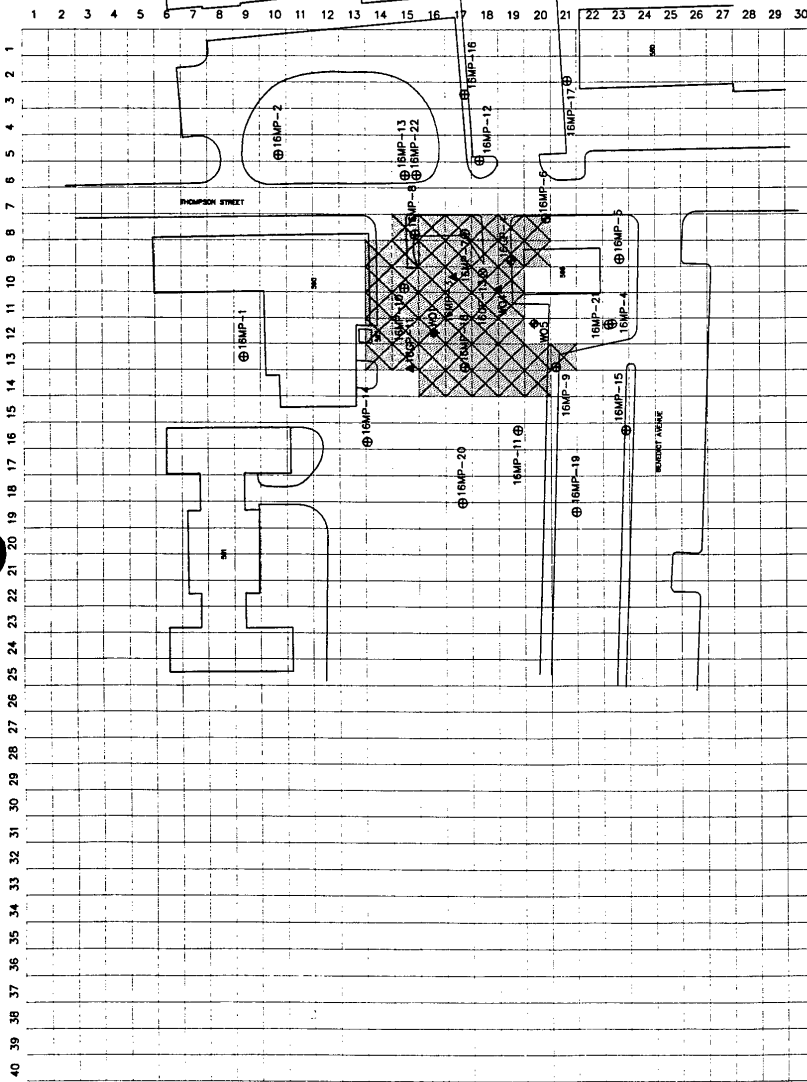
Seasonal variations in groundwater flow direction are not well documented. The observed groundwater flow direction at the site is unusual, in that groundwater in water table aquifers generally flow from recharge areas to discharge areas. Under natural conditions, the intuitive discharge point for shallow groundwater at the site is the Southwest Branch of the Back River, approximately 400 feet to the southeast. However, groundwater flow at the site flows parallel to the river to the southwest. Groundwater flows on site from higher heads near 16MP-16 and 16MP-17, and these higher heads may be a result of a mounded water table to the northeast. Hydraulic mounding may be expected within large, natural recharge areas (e.g., grass-covered fields), however no significant natural recharge areas are located in the vicinity of the apparent mound near 16MP-16 and 16MP-17. Mounding of the water table can also result from artificial recharge sources (e.g., leaky water mains, irrigation, etc.) and may be the cause for the elevated water table northeast of the site. The current water table configuration, however, appears to be relatively constant over time, as reflected in the distribution of dissolved BTEX concentrations in groundwater. Therefore, as described in Section 5.4.1, the model was calibrated to a reasonable match of the observed water table.

5.3.3 BTEX Concentrations

The total dissolved BTEX concentrations obtained from laboratory analytical results for each well and monitoring point location were used for model development. Table 4.2 presents dissolved BTEX concentration data. Figure 4.2 shows the areal distribution of dissolved BTEX compounds in shallow groundwater from July 1995. The suspected areal extent of residual contamination is estimated at 15,500 square-feet (0.35 acre). The estimated source strength from the residual LNAPL contamination was modeled using 44 simulated injection wells to maintain a mass balance without exceeding the constraints of the Bioplume II model. The 44 source wells coincide with the suspected areal extent of residual LNAPL contamination (Figure 5.2). The methods used to estimate the leaching potential of residual LNAPL to groundwater are described in Section 5.4.2. The injection volume for the injection wells was set at a rate low enough that the hydraulic calibration for the model was not affected.

Groundwater can become contaminated with BTEX when infiltrating precipitation percolates downward through residual LNAPL soil contamination and into groundwater. In addition, desorption of BTEX from saturated soils within the aquifer can also contribute to dissolved BTEX contamination.

In general, the petroleum-impacted soils at the site were found at and below the water table. However, limited shallow soil contamination above the water table was found at several locations beneath the parking lot between Buildings 590 and 596. The contribution to BTEX in groundwater from these unsaturated soils is likely minimal due to limited rainfall infiltration through the asphalt. The primary source of BTEX in groundwater was estimated to be the desorption of BTEX from residual LNAPL contamination beneath the water table. The initial distribution of the residual LNAPL source in the Bioplume II model was estimated from the July 1995 distribution of BTEX



LEGEND

- WOI MONITORING WELL
- 16MP-12 MONITORING POINT
- 16GP-11 GEOPROBE BORING
- CELL WITH SIMULATED INJECTION WELL

**FIGURE 5.2
LOCATIONS OF
SIMULATED INJECTION WELLS
FOR CALIBRATION
AND PREDICTION**

IRP SITE SS-16
INTRINSIC REMEDIATION TS
LANGLEY AFB, VIRGINIA

**PARSONS
ENGINEERING SCIENCE, INC.**
ATLANTA, GEORGIA

in soil and groundwater. These initial estimates were considered a starting point for the plume calibration process, and were iteratively varied to achieve an acceptable representation of the July 1995 BTEX plume.

5.3.4 Anaerobic Degradation Rates

Available data strongly suggest that anaerobic degradation is occurring at the site. Combined anaerobic processes account for over 94 percent of the expressed assimilative capacity of site groundwater (Table 4.6). Anaerobic degradation must therefore be simulated with Bioplume II to make meaningful predictions. The Bioplume II model simulates anaerobic biodegradation by assuming that such degradation follows first-order kinetics. As with a large number of biological processes, anaerobic biodegradation can generally be described using a first-order rate constant and the equation:

$$\frac{C}{C_0} = e^{-kt}$$

Where: C = Contaminant Concentration at Time t

C_0 = Initial Contaminant Concentration

k = Coefficient of Anaerobic Decay (anaerobic rate constant)

t = time

Two methods of calculating the anaerobic rate constant are currently available to quantify rates of biodegradation at the field scale and are applicable for use with available site data. The first method involves the use of a biologically recalcitrant compound found in the dissolved BTEX plume that can be used as a conservative tracer. The second method, proposed by Buscheck and Alcantar (1995) involves interpretation of a steady-state contaminant plume configuration and is based on the one-dimensional

steady-state analytical solution to the advection-dispersion equation presented by Bear (1979).

5.3.4.1 Trimethylbenzene Tracer Method

In order to calculate anaerobic rate constants, the apparent degradation rate must be normalized for the effects of dilution caused by advective-dispersive processes and sorption. This can be accomplished by normalizing the concentration of each contaminant to the concentration of a component of gasoline (a tracer) that has sorptive properties similar to those of the BTEX compounds but that is fairly recalcitrant to biodegradation. Observed BTEX concentration data can be normalized to the TMB isomers 1,3,5-TMB, 1,2,4-TMB, and/or 1,2,3-TMB or to another tracer with similar physiochemical properties, such as TEMB. The TMB and TEMB compounds can serve as good tracers because they can be recalcitrant under anaerobic conditions, and they have sorptive properties similar to the BTEX compounds (Cozzarelli *et al.*, 1990 and 1994). Thus, these compounds are assumed to respond similarly to the processes of advection, dispersion, and sorption without experiencing a reduction in concentration due to biodegradation. Because TMB and TEMB compounds are not completely recalcitrant and because they migrate more slowly than BTEX compounds, anaerobic decay rates calculated using this method are considered very conservative.

The corrected concentration of a compound is the concentration of the compound that would be expected at one point (B) located downgradient from another point (A) after correcting for the effects of dispersion, dilution, and sorption between points A and B. One relationship that can be used to calculate the corrected contaminant concentration is:

$$C_{B, \text{Corr}} = C_B (\text{TMB}_A / \text{TMB}_B)$$

Where: $C_{B, \text{Corr}}$ = Corrected concentration of compound at Point B

C_B = Measured concentration of compound at Point B

TMB_A = Measured TMB concentration at Point A

TMB_B = Measured TMB concentration at Point B.

A log-linear plot of the corrected contaminant concentrations versus the travel time from the origin can be used to determine whether the data set can be described using a first-order exponential equation [i.e., the coefficient of determination (r^2) is greater than approximately 0.9]. When this occurs, the exponential slope can be used as the anaerobic rate constant.

Application of the tracer method to the conditions encountered at IRP Site SS-16 presented some difficulties and does not result in a reliable value for the anaerobic decay rate. First, the anaerobic region of the plume is relatively small, and flow paths containing at least three wells and/or monitoring points could not be constructed without including wells in the aerobic portion of the plume. Secondly, consideration was given to calculation of an *estimated* anaerobic decay rate based on BTEX, TMB, and TMB results from two points within the anaerobic region. The flow path from 16MP-3 to W01 was the only plausible flow path available to consider. Examination of the relative BTEX concentrations from these wells, however, showed increasing BTEX concentrations with downgradient distance, therefore the anaerobic decay rate calculations were not performed. The increase in concentration is likely a result of a non-uniform distribution of BTEX in the unsaturated and saturated soils within the source area, which in turn result in a "non-classical" distribution of BTEX (i.e., increasing concentration with downgradient distance) in the shallow groundwater. Therefore, based on the unique environmental conditions encountered at the site, the anaerobic decay rate was not calculated using the TMB tracer method.

5.3.4.2 Method of Buscheck and Alcantar

Buscheck and Alcantar (1995) derive a relationship that allows calculation of first-order decay rate constants for steady-state plumes. This method involves coupling the regression of contaminant concentration (plotted on a logarithmic scale) versus distance downgradient (plotted on a linear scale) to an analytical solution for one-dimensional, steady-state, contaminant transport that includes advection, dispersion, sorption, and biodegradation. For a steady-state plume, the first-order decay rate is given by (Buscheck and Alcantar, 1995):

$$\lambda = \frac{v_c}{4\alpha_x} \left(\left[1 + 2\alpha_x \left(\frac{k}{v_x} \right) \right]^2 - 1 \right)$$

Where: λ = first-order decay rate

v_c = retarded contaminant velocity in the x-direction

α_x = dispersivity

k/v_x = slope of line determined from a log-linear plot of contaminant concentration versus distance downgradient along flow path.

The first-order decay rate includes biodegradation resulting from both aerobic and anaerobic processes; however, in the absence of oxygen, the first-order rate is equivalent to the anaerobic decay rate. Appendix D presents the first-order rate constant calculations for BTEX using July 1995 data for the site and the method proposed by Buscheck and Alcantar (1995). A southwesterly groundwater flow path through points W04, 16MP-18, and 16MP-20 was used for the prediction of a biodegradation rate. An exponential fit to the data estimates a log-linear slope of 0.0146 $\mu\text{g/L}$ per foot, which was in turn used to estimate a decay constant of 0.0020 day^{-1} . The loss of BTEX along this

flow path has a tolerable closeness-of-fit to a first-order biodegradation decay rate because the calculated r^2 was 0.89. A southwesterly flow path through W01 and 16MP-14 also was used to estimate the anaerobic decay constant. A value of 0.0039 day^{-1} was obtained from a log-linear best-fit slope of $0.0255 \text{ } \mu\text{g/L per foot}$.

5.3.4.3 Selection of Anaerobic Decay Rate Constant

A review of recent literature indicates that anaerobic rate constants higher than 0.002 day^{-1} , generally have been calculated at other sites. For example, Chapelle (1994) reported that at two different sites with anaerobic groundwater conditions, the anaerobic rate constants were both approximately 0.01 day^{-1} . Wilson *et al.* (1994) reported first-order anaerobic biodegradation rates of 0.05 to 1.3 week^{-1} (0.007 to 0.185 day^{-1}); Buscheck *et al.* (1993) report first-order attenuation rates in a range of 0.001 to 0.01 day^{-1} ; and Stauffer *et al.* (1994) report rate constants of 0.01 and 0.018 day^{-1} for benzene and *p*-xylene, respectively. An anaerobic rate constant of 0.003 day^{-1} (average of 0.0020 day^{-1} and 0.0039 day^{-1}) was used as a starting value in the calibration of the Bioplume II model for the site. Through iterative variation of the anaerobic decay coefficient and other select model parameters, the model was calibrated to the July 1995 analytical data. An anaerobic decay constant of 0.008 day^{-1} was used in the calibrated model. This value is slightly higher than the rates predicted by the method of Buscheck and Alcantar; however, 0.008 day^{-1} is at the low end of the range of values reported in the literature. Therefore, this selected biodegradation rate is potentially conservative.

5.4 MODEL CALIBRATION

Model calibration is an important component in the development of any numerical groundwater model. Calibration of the flow model demonstrates that the model is capable of matching hydraulic conditions observed at the site; calibration of a contaminant transport model superimposed upon the calibrated flow model helps verify that contaminant loading and transport conditions are being appropriately simulated. The

numerical flow model presented herein was calibrated by altering transmissivity and constant-head boundary conditions in a trial-and-error fashion until simulated heads approximated observed field values within a prescribed accuracy. After calibration of the flow model, the numerical transport model was calibrated by estimating and adjusting transport parameters in a trial-and-error fashion until the simulated BTEX plume approximated observed field values. Table 5.1 lists input parameters used for the modeling effort. Model input and output files are included in Appendix E.

5.4.1 Water Table Calibration

The shallow water table at IRP Site SS-16 was assumed to be influenced by continuous recharge and discharge at the constant-head cells surrounding the model grid. The initial water levels at the constant-head cells and the transmissivity values were varied to calibrate the water table surface. The model was calibrated under steady-state conditions.

Hydraulic conductivity is an important aquifer characteristic that determines the ability of the water-bearing strata to transmit groundwater. Transmissivity is the product of the hydraulic conductivity and the thickness of the aquifer. An accurate estimate of hydraulic conductivity is important to help quantify advective groundwater flow velocities and to define the flushing potential of the aquifer and the quantity of electron-acceptor-charged groundwater that is entering the site from upgradient locations. According to the work of Rifai *et al.* (1988), the Bioplume II model is particularly sensitive to variations in hydraulic conductivity. Lower values of hydraulic conductivity result in a slower-moving plume with a relatively small areal extent and higher average BTEX concentrations. Higher values of hydraulic conductivity result in a faster-moving plume that is spread over a larger area and contains lower average BTEX concentrations.

TABLE 5.1
BIOPLUME II MODEL INPUT PARAMETERS
 IRP SITE SS-16
 INTRINSIC REMEDIATION TS
 LANGLEY AFB, VIRGINIA

Parameter	Description	Calibrated Model Setup	GSW
NTIM	Maximum number of time steps in a pumping period	5	5
NPMP	Number of Pumping Periods	10	40
NX	Number of nodes in the X direction	30	30
NY	Number of nodes in the Y direction	40	40
NPMAX	Maximum number of Particles	10,800	10,800
NPNT	Time step interval for printing data	5	5
NITP	Number of iteration parameters	7	7
NUMOBS	Number of observation points	0	0
ITMAX	Maximum allowable number of iterations in ADIP ^{a/}	200	200
NREC	Number of pumping or injection wells	44	44
NPTPND	Initial number of particles per node	9	9
NCODES	Number of node identification codes	2	2
NPNTMV	Particle movement interval (IMOV)	0	0
NPNTVL	Option for printing computed velocities	0	0
NPNTD	Option to print computed dispersion equation coefficients	0	0
NPDELC	Option to print computed changes in concentration	0	0
NPNCHV	Option to punch velocity data	0	0
NREACT	Option for biodegradation, retardation and decay	1	1
PINT	Pumping period (years)	2	2
TOL	Convergence criteria in ADIP	0.001	0.001
POROS	Effective porosity	0.20	0.20
BETA	Characteristic length (long. dispersivity; feet)	15	15
S	Storage Coefficient	0 (Steady- State)	0 (Steady- State)
TIMX	Time increment multiplier for transient flow	-	-
TINIT	Size of initial time step (seconds)	-	-
XDEL	Width of finite difference cell in the x direction (feet)	18	18
YDEL	Width of finite difference cell in the y direction (feet)	18	18
DLTRAT	Ratio of transverse to longitudinal dispersivity	0.3	0.3
CELDIS	Maximum cell distance per particle move	0.5	0.5
ANFCTR	Ratio of Tyy to Txx (1 = isotropic)	1	1
DK	Distribution coefficient	0.067	0.067
RHOB	Bulk density of the solid (grams/cubic centimeter)	1.59	1.59
THALF	Half-life of the solute	-	-
DEC1	Anaerobic decay coefficient (day ⁻¹)	0.008	0.008
DEC2	Reaeration coefficient (day ⁻¹)		
F	Stoichiometric Ratio of Hydrocarbons to Oxygen	3.14	3.14

^{a/} ADIP = Alternating-direction implicit procedure (subroutine for solving groundwater flow equation)

Saturated thickness data from previous reports, geologic logs, and water level measurements were used in conjunction with the hydraulic conductivity estimates to create an initial transmissivity grid for the entire model. A uniform transmissivity of 1,050 square feet per day (ft²/day) was used across the entire model domain. Figure 5.3 shows the calibrated water table.

Water level elevation data from cells associated with 22 groundwater monitoring locations were used to compare measured and simulated heads for calibration. The 22 selected cell locations each contained one of the following monitoring points/wells: 16MP-1, 16MP-2, 16MP-4, 16MP-5, 16MP-6, 16MP-7, 16MP-8, 16MP-9, 16MP-10, 16MP-11, 16MP-12, 16MP-13, 16MP-14, 16MP-15, 16MP-16, 16MP-17, 16MP-18, 16MP-19, 16MP-20, W01, W04, and W05.

The root mean square (RMS) error is commonly used to express the average difference between simulated and measured heads. RMS error is the average of the squared differences between measured and simulated heads, and can be expressed as:

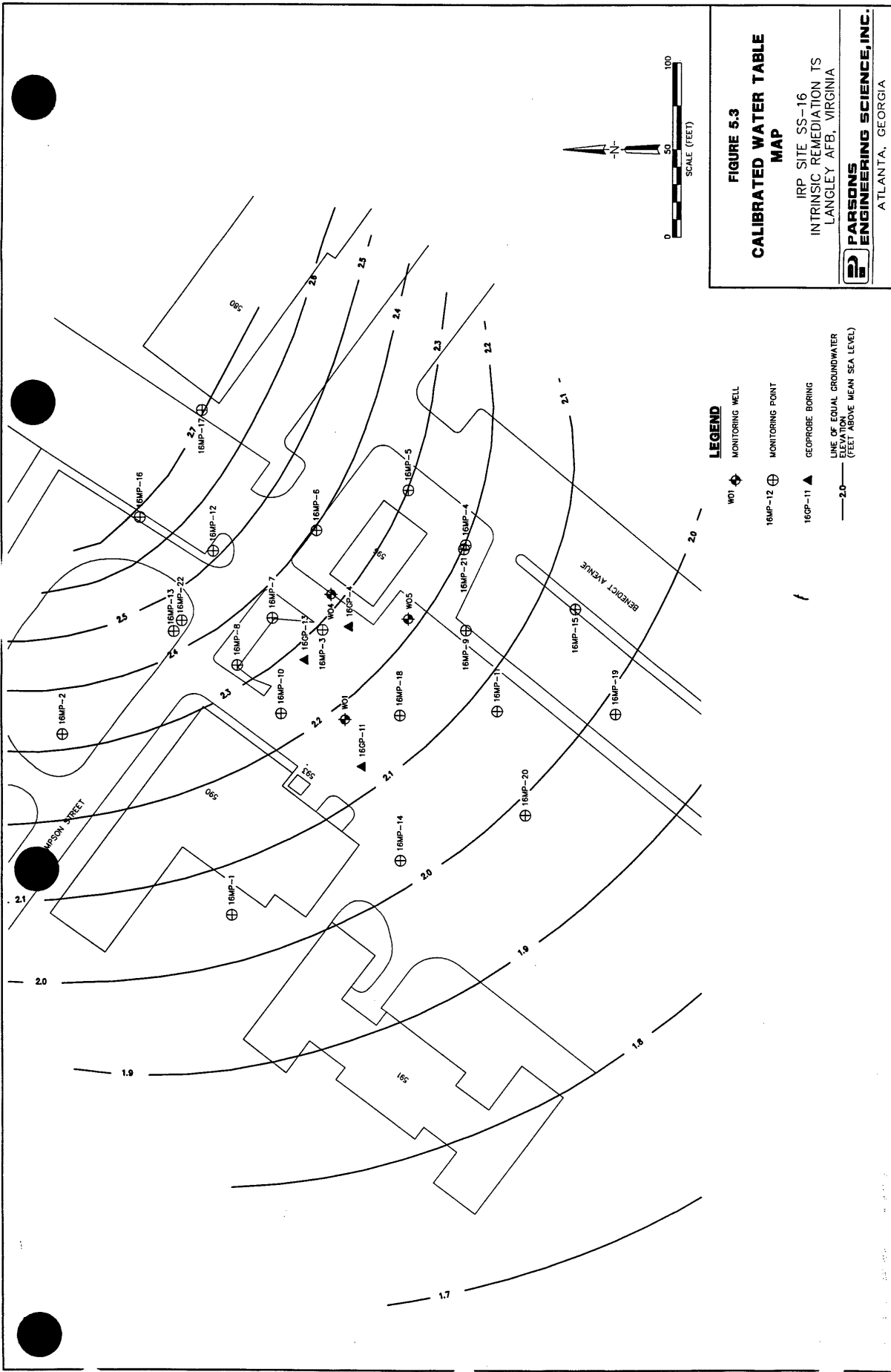
$$\text{RMS} = \left[\frac{1}{n} \sum_{i=1}^n (h_m - h_s)_i^2 \right]^{0.5}$$

Where: n = the number of points where heads are being compared

h_m = measured head value (feet above msl)

h_s = simulated head value (feet above msl)

The RMS error between observed and calibrated values at the 22 comparison points was 0.05 foot, which corresponds to a calibration error of 6.6 percent (water levels dropped 0.72 foot over the length of the model grid). RMS error calculations are summarized in Appendix D. A plot of measured versus calibrated heads shows a random



distribution of points around a straight line, as shown in Appendix D. Deviation of points from a straight line should be randomly distributed in such a plot of results from computer simulations (Anderson and Woessner, 1992). The largest deviations from the straight line occurred in the vicinity of the Building 596 (16MP-4, 16MP-5, and 16MP-6), where abrupt changes in groundwater flow direction were observed.

In solving the groundwater flow equation, Bioplume II establishes the water table surface and calculates an overall hydraulic balance that accounts for the numerical difference between flux into and out of the system. Considering the unusual groundwater hydraulics at the site, the hydraulic mass balance for the calibrated model was good, with 99.6-percent of the water flux into and out of the system being numerically accounted for (i.e., a 0.4-percent error). According to Anderson and Woessner (1992), a mass balance error of around 1 percent is acceptable, while Konikow (1978) indicates an error of less than 0.1 percent is ideal.

5.4.2 BTEX Plume Calibration

Model input parameters affecting the distribution and concentration of the simulated BTEX plume were modified so that model predictions matched dissolved total BTEX concentrations observed in July 1995. To do this, model runs were made using the calibrated steady-state hydraulic parameters coupled with the simulated introduction of contaminants. Because the exact time and frequency of the fuel release at the site is unknown, the model was calibrated to match July 1995 conditions, assuming that current observed conditions are a result of gradual weathering of residual LNAPL beneath the site.

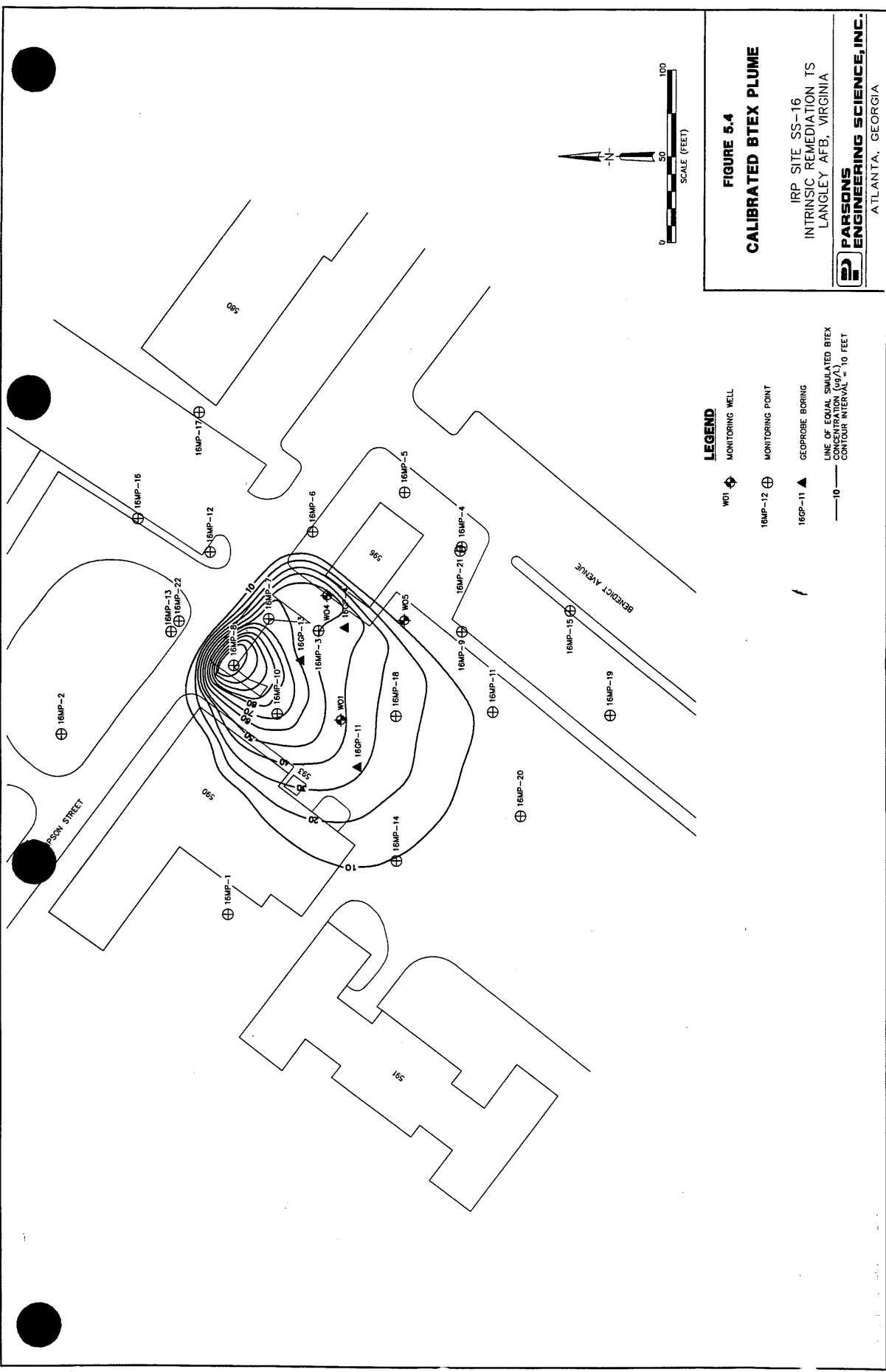
Estimated BTEX loading rates (Section 5.3.3) were applied to the 44 simulated injection wells of the model grid to reproduce the configuration and concentrations of the groundwater BTEX plume (Figure 5.2). While the term "injection well" suggests

contaminants are being introduced at a point, Bioplume II assumes that contamination introduced at a well instantly equilibrates throughout the entire cell in which the well is located. The injection rate for the cells was set at 2.14×10^{-7} cubic foot per second (ft^3/sec), a value low enough that the flow calibration and water balance was not affected. Loading rates were varied cell by cell as needed to reproduce the shape of the observed groundwater plume. The configuration of the BTEX plume beneath the grass island (at 16MP-7 and 16MP-8) and in the vicinity of W04 was calibrated by applying 91 percent of the BTEX source to nine of the grid cells in the area of residual LNAPL along Thompson Avenue and in the vicinity of the former UST immediately northwest of Building 596. The remaining 9 percent of the source strength was distributed to 35 grid cells within the remaining area of known residual LNAPL contamination. A higher BTEX source strength was estimated for the area along Thompson Avenue and near Building 596 because the highest BTEX concentration in soil and groundwater were detected in these areas (16MP-7 and 16MP-8, respectively). Furthermore, the recharge rate, thus BTEX leaching rate, is higher due to the absence of asphalt. The remainder of the residual LNAPL is located beneath the parking lot between Buildings 590 and 596. The contribution of BTEX to groundwater in this area is estimated to be significantly less due to the asphalt cover which virtually eliminates rainfall percolation and because the BTEX concentrations detected in soils from this area are lower in magnitude than those along Thompson Avenue.

Plume calibration was performed over a 20-year simulation period. Although records indicate that fuel was stored and transferred at the site as long as 60 years ago, no spills or leaks were documented in the records, and accurate simulation of the source strength, plume formation, and plume configuration over the past decades proved difficult. Therefore, a 20-year simulation period was assumed. Computed BTEX plume concentrations and configurations were compared to July 1995 BTEX data after 20 years

of simulation time incorporating injection, transport, and degradation of contaminants in groundwater. It was assumed that during the calibration simulation, injected BTEX concentrations would decrease at a conservative rate of 5 percent every 2 years. This assumption is plausible because mobile LNAPL (a continuous steady source of BTEX) was not found in any of the wells or monitoring points at the site. The primary source of BTEX in groundwater is the desorption of BTEX from saturated soils beneath the site. BTEX were detected in soils above the water table at two Geoprobe® locations: 16GP-3 (16MP-3) and 16GP-4. Both of these boring were installed in the asphalt parking lot. Significant contribution to dissolved BTEX in groundwater through leaching from these unsaturated soils is unlikely due to the relative impermeability of the asphalt cover. The calibrated plume is shown in Figure 5.4. The final calibrated model plume (year 20) was assumed to represent present-day (1995) conditions and compares favorably to the observed BTEX plume (Figure 4.2).

The objective of the calibration was to achieve a modeled plume that equaled or exceeded the observed plume in terms of extent and concentration, and that effectively simulated the predominant flow of BTEX contaminants to the southwest. The calibrated model successfully meets these objectives, as it reproduces both the observed areal extent and contaminant concentrations. The calibrated plume accurately predicts a predominant flow of contamination from the source area to the southwest. In general, the simulated BTEX concentrations were slightly higher than the observed values. Within the grass island adjacent to Thompson Avenue, the calibrated BTEX concentration of 130 µg/L slightly exceeds the observed BTEX concentration of 123 µg/L at 16MP-8. Near Building 596, the calibrated BTEX concentration of 53 µg/L at W04 is slightly lower than the observed concentration of 59 µg/L. The 10-µg/L contour approximated from observed BTEX concentrations is 140 feet long along the sothwest-northeast axis and roughly 120 feet wide along the southeast-northwest axis. In the model, the simulated



10- $\mu\text{g/L}$ contour is slightly larger, with length and width dimensions of 170 feet and 130 feet, respectively. In addition, the calibrated BTEX concentrations in the central portion of the source area (16MP-10, and 16MP-3) are higher than the observed values.

The fact that the model concentrations in the source area and along the downgradient plume edge are slightly higher than observed concentrations means that additional BTEX mass is included for in the model simulations, and that model predictions therefore are conservative. Variations in shape between the model and the observed plume likely are due to subsurface heterogeneities in the hydraulic conductivity, reaeration coefficient, dispersivity, and retardation coefficient that are extremely difficult to identify in the field and to replicate in a discretized model domain.

The solute fate and transport parameters varied during plume calibration were dispersivity and the coefficient of anaerobic decay. These parameters were generally varied with intent of altering plume migration so that the observed plume extent was reproduced. While these parameters were varied with this common intent, each had a slightly different impact on the size and shape of the simulated plume.

5.4.2.1 Dispersivity

Much controversy surrounds the concepts of dispersion and dispersivity. Longitudinal dispersivity values for sediments similar to those found at the site range from 0.1 to 200 feet (Walton, 1988). Longitudinal dispersivity was estimated as 15 feet, using approximately one-tenth (0.1) of the length of the plume (see Figure 4.3). Transverse dispersivity values are typically in the range of one-twentieth (0.05) to one-fifth (0.2) of the longitudinal dispersivity values (Freeze and Cherry, 1979).

During plume calibration, longitudinal dispersivity was maintained at 15 feet. The ratio of transverse dispersivity to longitudinal dispersivity was maintained at 0.3. This

ratio was maintained at a slightly higher value than the recommended range of values (Freeze and Cherry, 1979) to help reproduce the plume width observed at the site.

5.4.2.2 Coefficient of Retardation

Retardation of the BTEX compounds relative to the advective velocity of the groundwater occurs when BTEX molecules are sorbed to the aquifer matrix. The coefficients of retardation for the BTEX compounds were calculated based on measured TOC concentrations in the soils in and near the saturated zone at the site, an assumed bulk density of 1.59 grams per cubic centimeter (g/cc) (Freeze and Cherry, 1979), and published values of the soil sorption coefficients (K_{oc}) for the BTEX compounds, as listed by Wiedemeier *et al.* (1995). The results of these calculations are summarized in Table 5.2.

TOC analyses often are influenced by the presence of soil contamination, which may cause high soil TOC concentrations without necessarily reflecting an increase in the sorptive potential of soil. Therefore, TOC measurements used for retardation estimates should be taken from contaminant-free soils. Furthermore, TOC samples should be taken across the phreatic surface rather than in the vadose zone to best represent the sorptive potential of saturated soils in the aquifer. Five locations were chosen for TOC analyses at IRP Site SS-16 (Table 4.1). Of these five sampling locations, three were located outside of known residual LNAPL contamination and include: 16MP-1, 16MP-2, and 16MP-5 (Figure 4.1). All three of these samples were collected below the phreatic surface. TOC concentrations from these three locations ranged from less than 0.07 to 0.15 percent. Soil sampling location 16MP-1 exhibited the lowest TOC value. The average TOC concentration of the three samples (assuming one-half of the detection limit at 16MP-1) was 0.085 percent. Table 5.2 reflects the use of this average TOC concentration to estimate the retardation potential in the aquifer. A final value of 1.53 for the retardation coefficient was used for the BTEX compounds, and is intended to be

TABLE 5.2
CALCULATION OF RETARDATION COEFFICIENTS
IRP SITE 16
INTRINSIC REMEDIATION TS
LANGLEY AFB, VIRGINIA

Compound	K_{oc} (L/kg ^{a/})	Maximum Fraction Organic Carbon ^{b/}	Minimum Fraction Organic Carbon ^{b/}	Average Fraction Organic Carbon ^{b/}	Distribution Coefficient K_d (L/kg)		Bulk Density (kg/L) ^{d/}	Effective Porosity ^{e/}	Coefficient of Retardation	
					Maximum ^{c1/}	Minimum ^{c2/} Average ^{c3/}			Maximum	Average
Benzene	79	0.0015	0.00035	0.00085	0.119	0.028 0.067	1.59	0.20	1.94	1.22
Toluene	190	0.0015	0.00035	0.00085	0.285	0.067 0.162	1.59	0.20	3.27	1.53
Ethylbenzene	468	0.0015	0.00035	0.00085	0.702	0.164 0.398	1.59	0.20	6.58	2.30
m-xylene	405	0.0015	0.00035	0.00085	0.608	0.142 0.344	1.59	0.20	5.83	2.13
o-xylene	422	0.0015	0.00035	0.00085	0.633	0.148 0.359	1.59	0.20	6.03	2.17
p-xylene	357	0.0015	0.00035	0.00085	0.536	0.125 0.303	1.59	0.20	5.26	1.99

NOTES:

^{a/} From technical protocol (Wiedemeier *et al.*, 1995)^{b/} From laboratory analyses of site soil samples; minimum value is one-half of the detection limit of 0.07%^{c1/} K_d = Maximum Fraction Organic Carbon x K_{oc} ^{c2/} K_d = Minimum Fraction Organic Carbon x K_{oc} ^{c3/} K_d = Average Fraction Organic Carbon x K_{oc} ^{d/} From laboratory analyses of moisture content, and assumed porosity and specific gravity.^{e/} Literature value (Johnson, 1967).

reflective of benzene, which is the least sorptive BTEX compound. During plume calibration, the initial coefficient of retardation was not changed.

5.4.2.3 Coefficient of Anaerobic Decay

The coefficient of anaerobic decay is a first-order rate constant used in Bioplume II to simulate the rate of use and replenishment of anaerobic electron acceptors in the groundwater. A coefficient of anaerobic decay of 0.002 day^{-1} was originally estimated, based on the method of Buscheck and Alcantar (1995). Use of an anaerobic decay coefficient is justified at this site because anaerobic decay mechanisms account for 94 percent of the biodegradation at the site. The coefficient of anaerobic decay had a significant effect on limiting plume migration, and was also important in controlling the concentrations at the fringes of the plume. Through the calibration process, the anaerobic decay coefficient was increased to a value of 0.008 day^{-1} to control the downgradient edge of the plume. Although the calibrated value was higher than initially estimated using the methods of Buscheck and Alcantar (1995), an anaerobic decay constant value of 0.008 day^{-1} is lower than typical values listed in literature, and is therefore considered reasonably conservative.

5.5 SENSITIVITY ANALYSIS

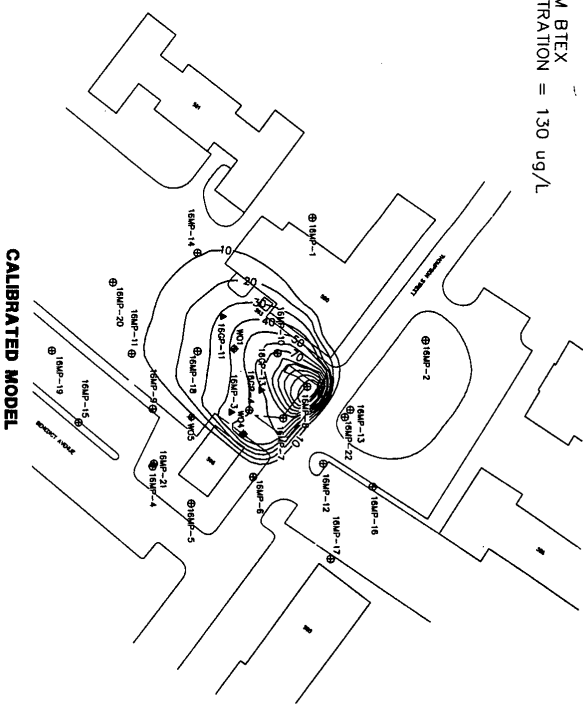
The purpose of the sensitivity analysis is to determine the effect of varying model input parameters on model output. Based on the work of Rifai *et al.* (1988), the Bioplume II model is most sensitive to changes in the coefficient of aerobic decay (reaeration coefficient), the coefficient of anaerobic decay, and the hydraulic conductivity of the media, and is less sensitive to changes in the retardation factor, porosity, and dispersivity. To fully evaluate the sensitivity of the calibrated model, the transmissivity, the coefficient of anaerobic decay, the coefficient of retardation, dispersivity, and porosity were all varied.

To perform the sensitivity analyses, the calibrated model was adjusted by systematically changing the aforementioned parameters individually, and then comparing the new model runs to the original calibrated model. The sensitivity models were run for a 20-year period (the same duration used for the original calibrated model) to assess the independent effect of each variable. To accomplish this assessment, 10 sensitivity runs of the calibrated model were made, with the following variations:

- 1) Transmissivity uniformly increased by a factor of 2;
- 2) Transmissivity uniformly decreased by a factor of 2;
- 3) Coefficient of anaerobic decay increased by a factor of 2;
- 4) Coefficient of anaerobic decay decreased by a factor of 2;
- 5) Coefficient of retardation increased by 20 percent;
- 6) Coefficient of retardation decreased by 20 percent;
- 7) Dispersivity increased by 50 percent;
- 8) Dispersivity decreased by 50 percent;
- 9) Porosity increased by 25 percent; and
- 10) Porosity decreased by 25 percent.

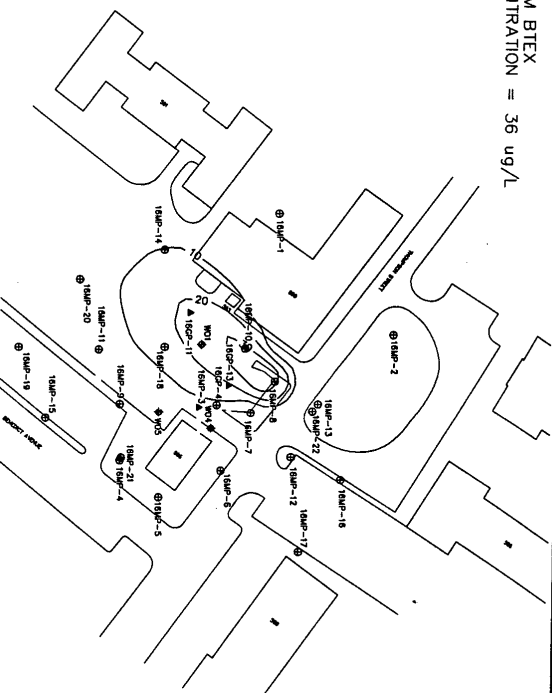
The results of the sensitivity analyses are shown graphically in Figures 5.5 through 5.9. The effects of varying transmissivity are shown on Figure 5.5. Uniformly increasing the transmissivity by a factor of two increased both the groundwater velocity and thus, the volumetric flow rate through water table aquifer. As a result, BTEX concentrations decreased in concentration throughout the plume by the following

MAXIMUM BTEX
CONCENTRATION = 130 ug/L



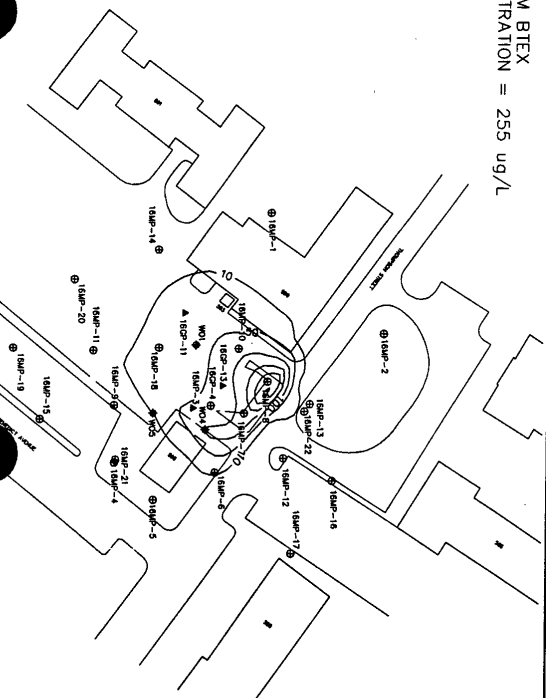
CALIBRATED MODEL

MAXIMUM BTEX
CONCENTRATION = 36 ug/L



TRANSMISSIVITY INCREASED 2X

MAXIMUM BTEX
CONCENTRATION = 255 ug/L



TRANSMISSIVITY DECREASED 2X

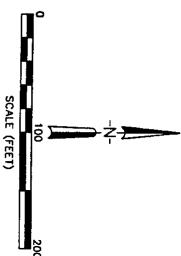


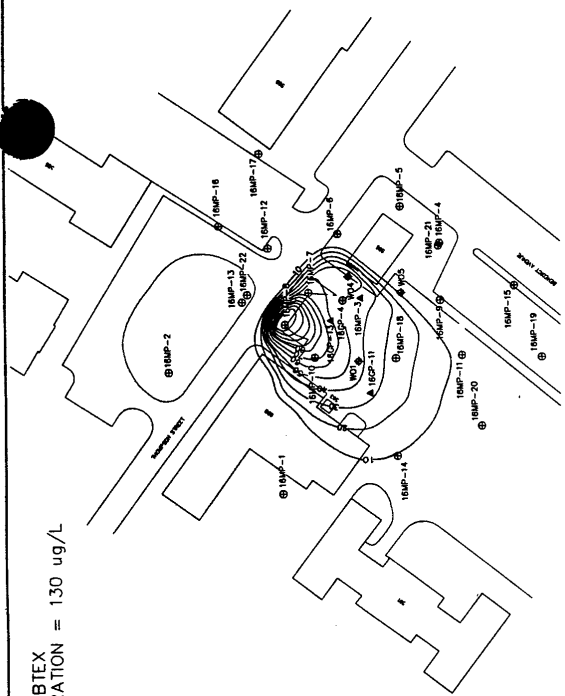
FIGURE 5.5
MODEL SENSITIVITY TO
VARIATIONS IN TRANSMISSIVITY

IRP SITE SS-16
INTRINSIC REMEDIATION TS
LANGLEY AFB, VIRGINIA

PARSONS
ENGINEERING SCIENCE

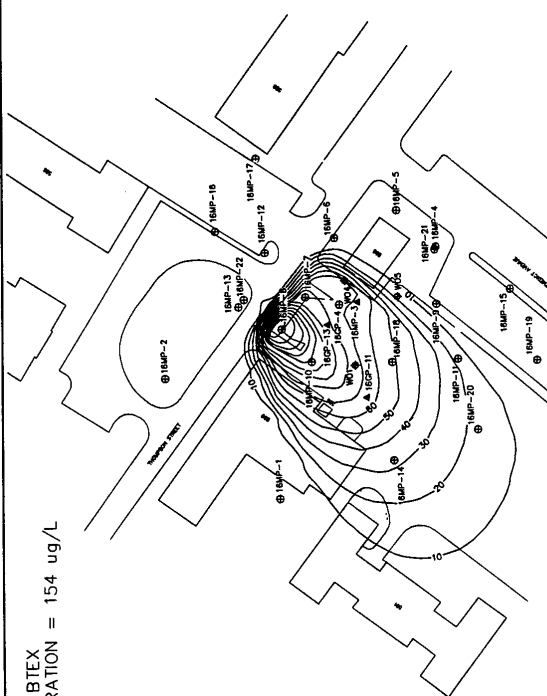
ATLANTA, GEORGIA

MAXIMUM BTX
CONCENTRATION = 130 ug/L



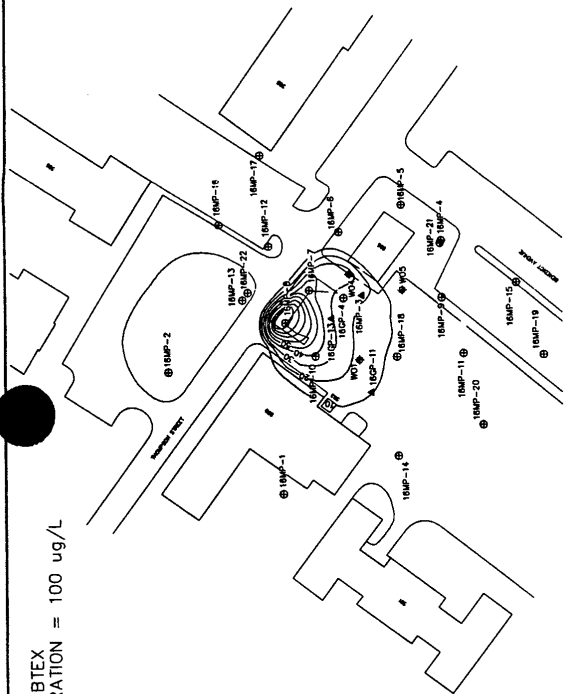
CALIBRATED MODEL

MAXIMUM BTX
CONCENTRATION = 154 ug/L



COEFFICIENT OF ANAEROBIC DECAY DECREASED 2X

MAXIMUM BTX
CONCENTRATION = 100 ug/L



COEFFICIENT OF ANAEROBIC DECAY INCREASED 2X

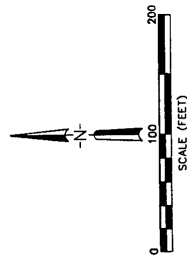


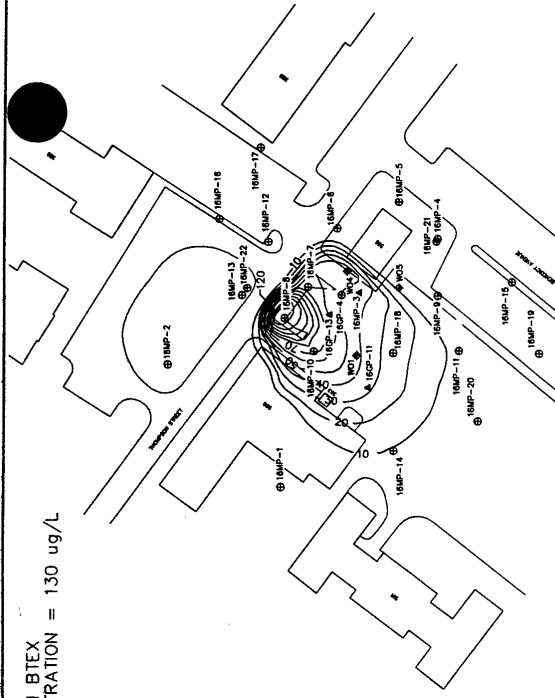
FIGURE 5.6

MODEL SENSITIVITY TO
VARIATIONS IN THE COEFFICIENT
OF ANAEROBIC DECAY

IRP SITE SS-16
INTRINSIC REMEDIATION TS
LANGLEY AFB, VIRGINIA

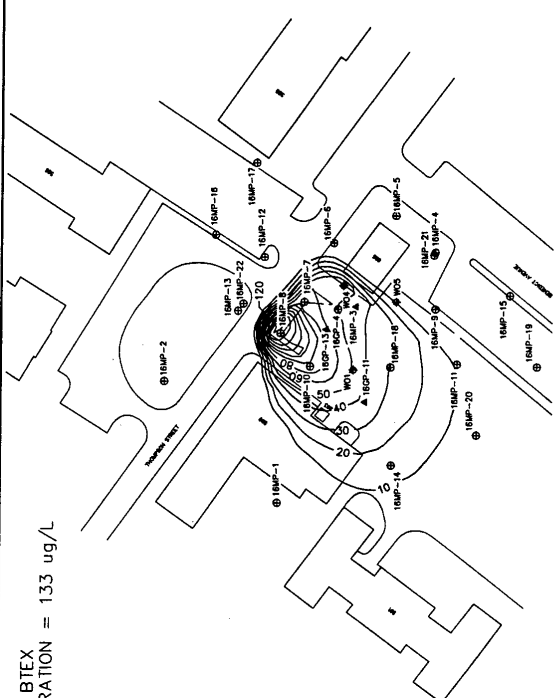
PARSONS
ENGINEERING SCIENCE, INC.
ATLANTA, GEORGIA

MAXIMUM BTX
CONCENTRATION = 130 ug/L



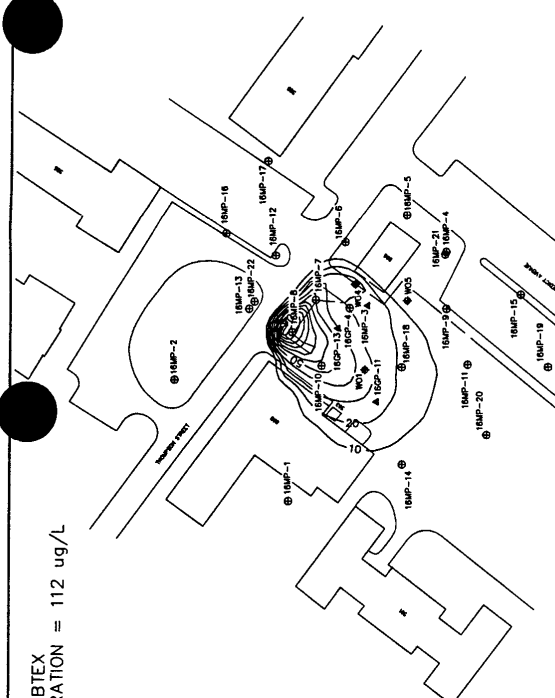
CALIBRATED MODEL

MAXIMUM BTX
CONCENTRATION = 133 ug/L



COEFFICIENT OF RETARDATION DECREASED BY 20 PERCENT

MAXIMUM BTX
CONCENTRATION = 112 ug/L



COEFFICIENT OF RETARDATION INCREASED BY 20 PERCENT

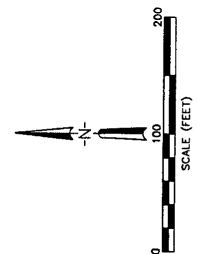
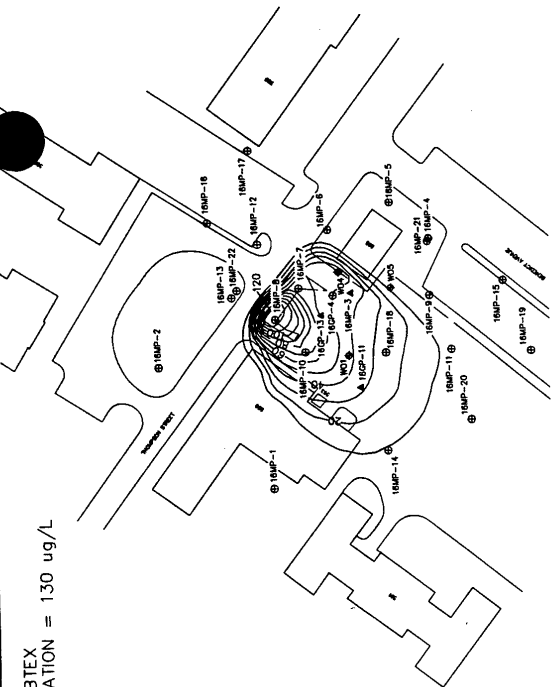


FIGURE 5.7
MODEL SENSITIVITY TO VARIATIONS IN THE COEFFICIENT OF RETARDATION
 IRP SITE SS-16
 INTRINSIC REMEDIATION TS
 LANGLEY AFB, VIRGINIA

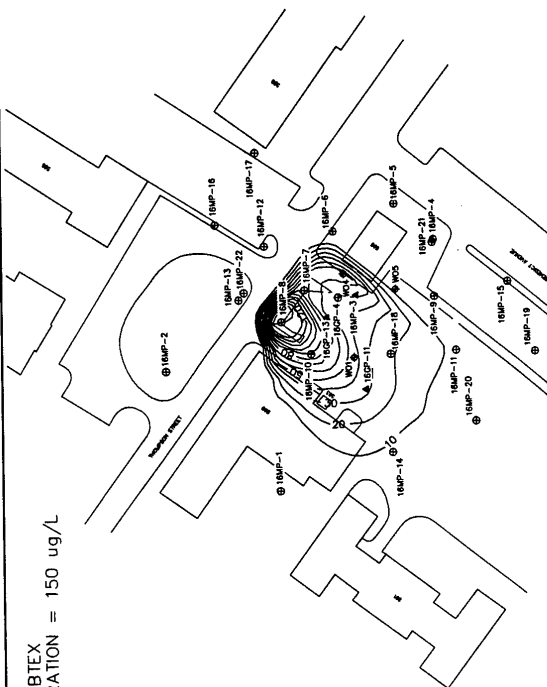
PARSONS ENGINEERING SCIENCE, INC.
 ATLANTA, GEORGIA

MAXIMUM BTX
CONCENTRATION = 130 ug/L



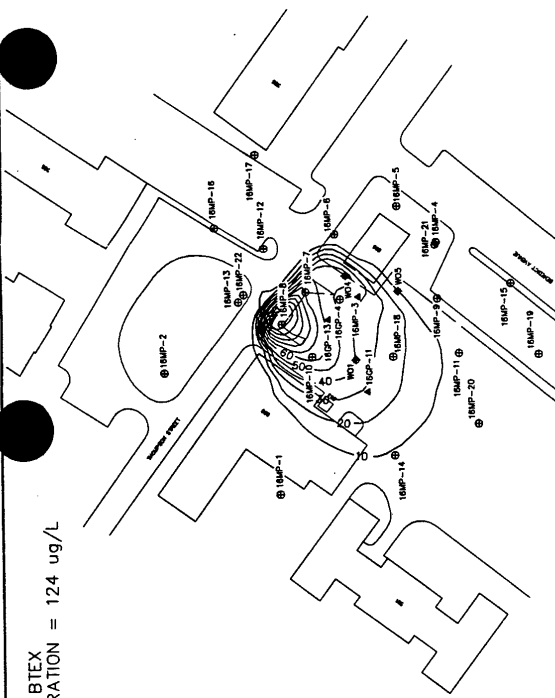
CALIBRATED MODEL

MAXIMUM BTX
CONCENTRATION = 150 ug/L

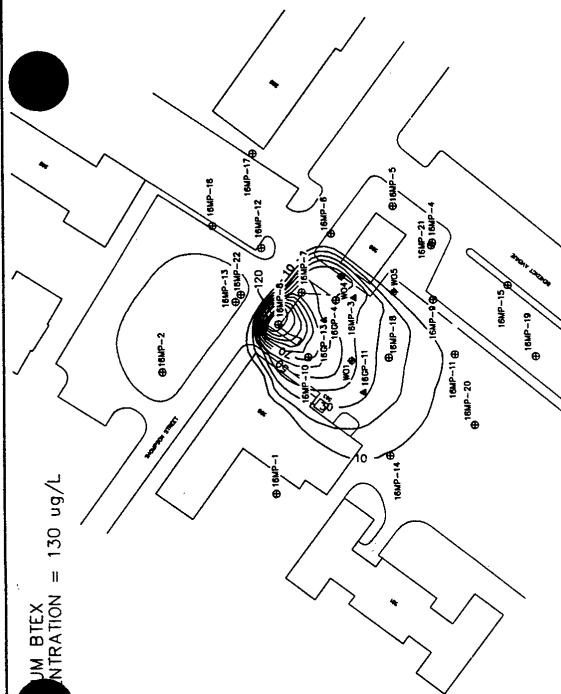


DISPERSIVITY DECREASED BY 50 PERCENT

MAXIMUM BTX
CONCENTRATION = 124 ug/L

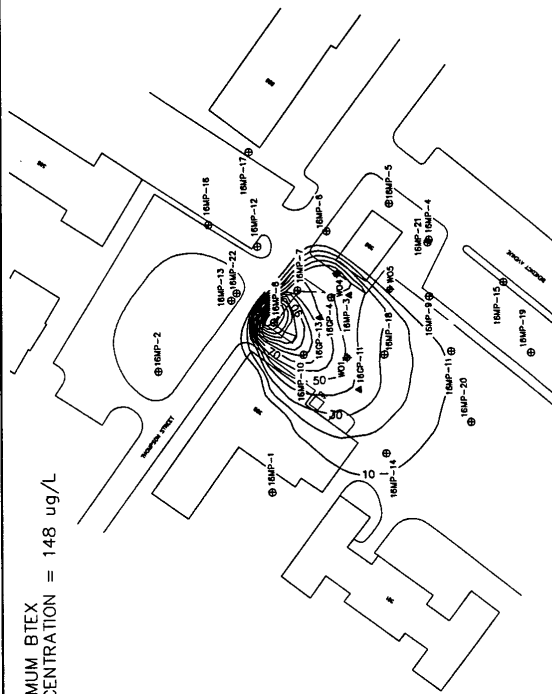


MAXIMUM BTEX
CONCENTRATION = 130 ug/L



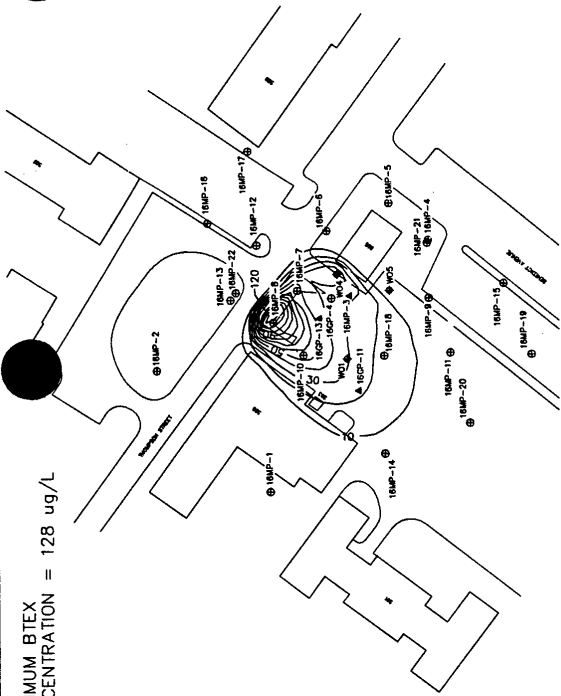
CALIBRATED MODEL

MAXIMUM BTEX
CONCENTRATION = 148 ug/L



POROSITY DECREASED BY 25 PERCENT

MAXIMUM BTEX
CONCENTRATION = 128 ug/L



POROSITY INCREASED BY 25 PERCENT

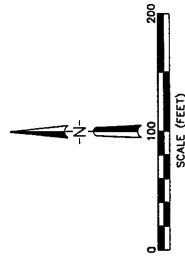


FIGURE 5.9

MODEL SENSITIVITY TO VARIATIONS IN POROSITY

IRP SITE SS-16
INTRINSIC REMEDIATION TS
LANGLEY AFB, VIRGINIA

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mechanisms. First, the BTEX concentrations are diluted due to the increased groundwater flux beneath the site. Second, BTEX concentrations may biodegrade more rapidly because of the increased influx of electron acceptors, such as DO, from upgradient sources. Under this scenario for transmissivity, the maximum observed BTEX concentration in the source area was 36 $\mu\text{g/L}$, compared to the calibrated maximum of 130 $\mu\text{g/L}$. In contrast, decreasing the transmissivity by a factor of two slowed overall plume migration, which increased the maximum BTEX concentrations because of decreased dilution rates and decreased influx of upgradient electron receptors. BTEX in the source area increased to approximately 255 $\mu\text{g/L}$, compared to the calibrated 130 $\mu\text{g/L}$. The sensitivity of the model to hydraulic conductivity suggests that an appropriate range of transmissivity values were used in the model calibration.

The effects of varying the coefficient of anaerobic decay are illustrated on Figure 5.6. Increasing this parameter by a factor of two results in an expected smaller plume with a maximum BTEX concentration of 100 $\mu\text{g/L}$. The outer fringe the BTEX plume also recedes as a result of increased biodegradation rates. Conversely, decreasing the coefficient of anaerobic decay by a factor of two decreases biodegradation and increases plume concentrations. The resultant increase raised computed maximum BTEX concentrations in the source area from 130 $\mu\text{g/L}$ to 154 $\mu\text{g/L}$ and resulted in advancement of the downgradient edge of the BTEX plume. These results show that the calibrated model is sensitive to variations in the coefficient of anaerobic decay and suggest that an appropriate value for the anaerobic decay coefficient was used in the calibrated model.

The effects of varying the coefficient of retardation (R) are shown on Figure 5.7. Increasing R by 20 percent has a minor effect on the contaminant distribution. An increase in sorptive capacity caused a decrease of approximately 18 $\mu\text{g/L}$ in the source

area leaving the maximum BTEX concentration at 112 $\mu\text{g/L}$. The decrease in plume concentrations resulted from a slowing of BTEX migration, which allowed for greater contact of the sorbed BTEX with electron acceptors introduced in upgradient and infiltration waters flushing through the system. Decreasing R by 20 percent decreases the potential for contact of sorbed BTEX with replenished electron acceptors, thus allowing less biodegradation. As a result, the maximum BTEX concentration in the source area increased to 133 $\mu\text{g/L}$ with a slight advancement of the downgradient edge of the plume. Because the retardation factor used for the model is low relative to other possible retardation factors (Table 5.2), the R used for the calibrated simulation is conservative and produced acceptable results.

The effects of varying dispersivity are illustrated on Figure 5.8. Both longitudinal and transverse dispersivity were varied for this analysis, as the ratio of the two values was kept constant at 0.3. Increasing the dispersivity by 50 percent resulted in a minor decrease in the maximum BTEX concentrations (by approximately 6 $\mu\text{g/L}$) without a noticeable change in areal extent of the plume. Decreasing the dispersivity by 50 percent produced a plume with slightly higher BTEX concentrations (by approximately 20 $\mu\text{g/L}$) without a noticeable change in areal extent. This model appears to be relatively insensitive to dispersivity within the range of reasonable values evaluated for this analysis.

The effects of varying the effective porosity are illustrated on Figure 5.9. Walton (1988) gives a range of 0.1 to 0.3 for the effective porosity of fine sand. Increasing the effective porosity by 25 percent resulted in a very minor decrease in the maximum BTEX concentrations (by approximately 2 $\mu\text{g/L}$) with a minor recedence of the downgradient plume fringe. Decreasing the effective porosity by 25 percent produced a plume with slightly higher BTEX concentrations (by approximately 18 $\mu\text{g/L}$) with minor

advancement of the downgradient plume fringe. Therefore, the model is slightly sensitive to the range of selected values used for effective porosity.

The results of the sensitivity analyses suggest that the calibrated model parameters used for this report are appropriate. The calibrated model is very sensitive to transmissivity and coefficient of anaerobic decay, slightly sensitive to effective porosity and retardation coefficient, and insensitive to dispersivity. Increasing the transmissivity and the coefficient of anaerobic decay greatly diminishes the predicted maximum BTEX concentrations, although only the coefficient of anaerobic decay results in an actual destruction of (decrease in) the mass of BTEX. Lowering the transmissivity or the coefficient of anaerobic decay has a reverse effect, and source area concentrations of BTEX in the aquifer are greatly increased. Decreases in effective porosity resulted in increases in maximum simulated BTEX concentrations and slight increases in the area of the plume. Increases in this parameter resulted in the opposite response. Decreases in retardation coefficient resulted in slight increases in maximum simulated BTEX concentrations and slight increases in the area of the plume. Increases in the retardation coefficient resulted in decreases in the maximum simulated BTEX concentration. The model appears relatively insensitive to dispersivity; however, calculation of values for this parameter contributed to an appropriate calibrated plume configuration.

5.6 MODEL RESULTS

To predict fate and transport of dissolved BTEX compounds at IRP Site SS-16, a single Bioplume II simulation (GSW) was completed. Run GSW (for Gradual Source Weathering) was used to realistically evaluate the migration and biodegradation of the BTEX plume assuming physical weathering of the source area. Physical weathering included desorption of BTEX from saturated residual LNAPL contamination into groundwater and from BTEX dissolution into infiltrating precipitation that contacts residual LNAPL contamination. This model does not account for volatilization of BTEX

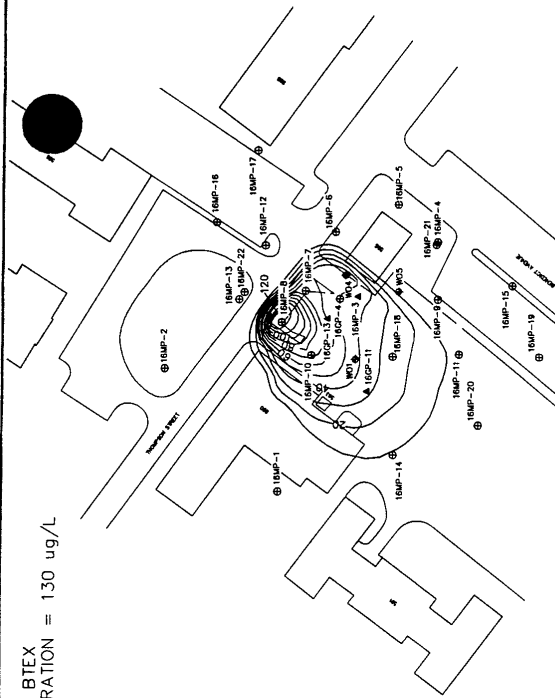
in the vadose zone, or microbial weathering of residual product remaining in site soils. Therefore, estimates of source reduction are conservative, which in turn result in conservative model predictions for plume migration. The BTEX loading rate was reduced by 5 percent every 2 years, which is consistent with the reduction rates assumed in the calibration of the model to the July 1995 plume.

In order to simulate the anticipated decrease in the source strength and composition, model GSW utilizes 40 pumping periods. The first 10 pumping periods (i.e., 20 years) are a copy of the calibrated model. Each of the successive pumping periods (11 through 40) has a duration of 2 years and assumes a BTEX injection rate lower than the previous period as a result of weathering. Following 40 years of physical weathering, the 2035 source strength is approximately 36 percent of the 1995 source strength.

Figure 5.10 shows the calibrated plume, the modeled plume for 2015 (20 additional years of simulated source weathering time) and the modeled plume for 2035 (40 years of additional simulation). After 20 years, modeled BTEX contours have noticeably changed in comparison to the 1995 calibrated model (Figure 5.10). Most isocontours have receded considerably, and the maximum BTEX concentration has decreased to 50 $\mu\text{g/L}$. The modeled 2035 plume (40 years of weathering) shows a drastic reduction in the plume extent and BTEX concentration. The maximum BTEX concentration in the source area (near 16MP-8) is approximately 16 $\mu\text{g/L}$. After approximately 50 years of natural weathering, the BTEX plume is reduced to concentrations of less than 1 $\mu\text{g/L}$.

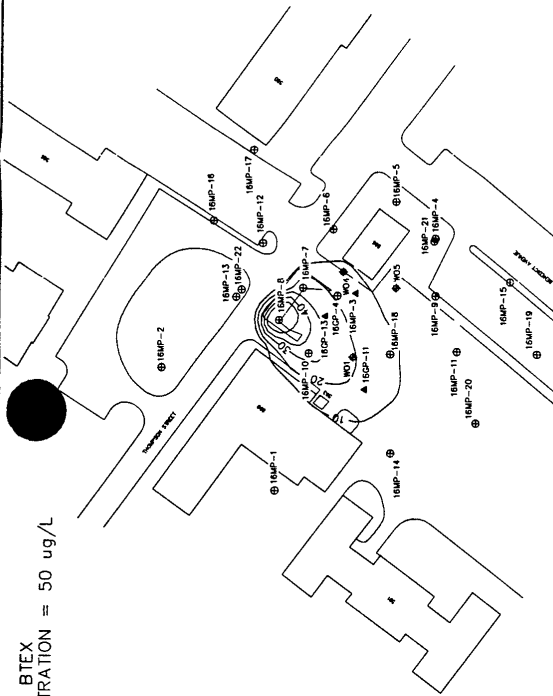
These results suggest that the observed BTEX plume may potentially decrease at considerable rates over the next 40 to 50 years. Through predictive modeling, natural attenuation mechanisms have been shown to effectively remove the remaining concentrations of BTEX from the aquifer at IRP Site 16.

MAXIMUM BTEX
CONCENTRATION = 130 ug/L



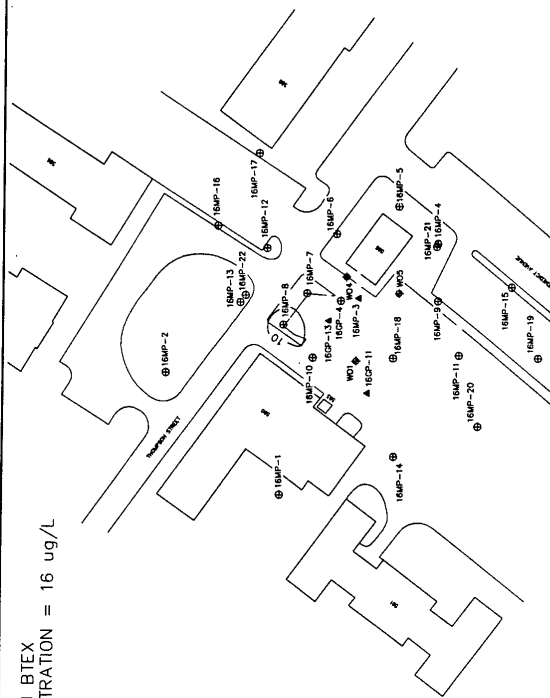
CALIBRATED MODEL (1985)

MAXIMUM BTEX
CONCENTRATION = 50 ug/L



20 YEARS OF WEATHERING (2015)

MAXIMUM BTEX
CONCENTRATION = 16 ug/L



40 YEARS OF WEATHERING (2035)

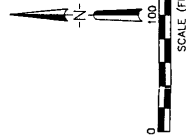


**FIGURE 5.10
PREDICTED PLUME MIGRATION
MODEL GSW**

IRP SITE SS-16
INTRINSIC REMEDIATION TS
LANGLEY AFB, VIRGINIA



**PARSONS
ENGINEERING SCIENCE, INC.**
ATLANTA, GEORGIA

5.7 CONCLUSIONS AND DISCUSSION

A single conservative model scenario was used to predict BTEX attenuation and migration rates at IRP Site SS-16. Model GSW assumed natural, physical weathering of the residual LNAPL in soil (leaching and desorption). The results of the Model GSW suggest that dissolved BTEX will naturally attenuate to undetectable levels over the next 40 to 50 years. The GSW model predicts that the leading edge of the plume will not advance further downgradient, and will recede as intrinsic remediation of dissolved BTEX in groundwater proceeds.

Several conservative assumptions are built into the model. The use of these conservative model assumption suggests that natural attenuation of BTEX contamination at the site may exceed model predictions. These conservative model assumptions include:

- 1) The stoichiometry used to determine the ratio between electron acceptors and total BTEX assumed that no microbial cell mass was produced during the reactions. As discussed in Section 4.3.2, this approach may be too conservative by a factor of three.
- 2) A low coefficient of retardation for benzene (1.53) was used for all the BTEX compounds in the model simulations. Average retardation coefficient values for the other BTEX compounds range from 2.28 to 4.16. The use of a conservative retardation coefficient tends to increase the velocity of contaminant migration, but may provide a more accurate estimate for benzene transport. However, realistic retardation coefficients for toluene, ethylbenzene, and xylenes are higher than that for benzene, which will slow the migration of these compounds, thereby increasing their susceptibility to biodegradation.

- 3) Calibrated source concentrations in the models were higher than observed concentrations. This introduction of extra contaminant mass likely results in the predictions being conservative because additional BTEX mass must be biodegraded to produce the observed results.

The model simulation results demonstrate the potential for intrinsic remediation to naturally attenuate the BTEX plume at the site without engineered removal or treatment of the impacted medias.

SECTION 6

COMPARATIVE ANALYSIS OF REMEDIAL ALTERNATIVES

This section presents the development and comparative analysis of groundwater remedial alternatives for IRP Site SS-16 at Langley AFB. The intent of this evaluation is to determine if intrinsic remediation for groundwater is an appropriate and cost-effective remedial approach to consider when developing final remedial strategies for the site.

Section 6.1 presents the criteria used to evaluate groundwater remedial alternatives. Section 6.2 discusses the development and comparative analysis of remedial alternatives considered as part of this demonstration project. Section 6.3 provides a description of the selected remedial alternative(s). Section 6.4 provides a more detailed evaluation of the selected remedial alternative(s) using the defined remedial alternative evaluation criteria.

6.1 REMEDIAL ALTERNATIVE EVALUATION CRITERIA

The evaluation criteria used to identify appropriate remedial alternatives for shallow groundwater contamination at the site were adapted from those recommended by the USEPA (1988) for selecting remedies for Superfund sites [Office of Solid Waste and Emergency Response (OSWER) Directive 9355.3-01]. These criteria included (1) long-term effectiveness and permanence, (2) technical and administrative implementability, and (3) relative cost. The following sections briefly describe the scope and purpose of each evaluation criterion. This report focuses on the potential use of intrinsic remediation to reduce BTEX concentrations in the shallow groundwater to levels that meet regulatory action levels.

6.1.1 Long-Term Effectiveness and Permanence

Each remedial technology or remedial alternative (which can be a combination of remedial approaches and technologies such as intrinsic remediation and institutional controls) was analyzed to determine how effectively it will minimize groundwater plume expansion so that groundwater quality standards can be achieved at a downgradient POC. The expected technical effectiveness based on case histories from other sites with similar conditions also is evaluated. The ability to minimize potential impacts to surrounding facilities and operations is considered. Also, the ability of each remedial alternative to protect both current and potential future receptors from potential risks associated with potential exposure pathways is qualitatively assessed. This evaluation criterion also included permanence and the ability to reduce contaminant mass, toxicity, and volume. Time to implementation and time until protection is achieved are described. Long-term reliability for providing continued protection, including an assessment of potential for failure of the technology and the potential threats resulting from such a failure, is also evaluated.

6.1.2 Implementability

The technical implementation of each remedial option or remedial alternative was evaluated in terms of technical feasibility and availability. Potential shortcomings and difficulties in construction, operations, and monitoring are presented and weighed against perceived benefits. Requirements for any post-implementation site controls such as LTM and land use restrictions are described. Details on administrative feasibility in terms of the likelihood of public acceptance and the ability to obtain necessary approvals are discussed.

6.1.3 Cost

The total cost (adjusted to present worth) of each remedial alternative was estimated for relative comparison. An estimate of capital costs, and operating and post-implementation costs for site monitoring and controls is included. An annual adjustment factor of 7 percent was assumed in present worth calculations. The annual adjustment factor is the difference between the rate of inflation and the cost of money (USEPA, 1993).

6.2 FACTORS INFLUENCING ALTERNATIVES DEVELOPMENT

Several factors were considered during the identification and screening of remedial options for addressing shallow groundwater contamination at the site. Factors considered included the objectives of the AFCEE natural attenuation demonstration program; contaminant, groundwater, and soil properties; current and future land uses; and potential receptors and exposure pathways. The following section briefly describes each of these factors and how they were used to narrow the list of potentially applicable remedial techniques to the final remedial alternatives considered for IRP Site SS-16.

6.2.1 Program Objectives

The intent of the intrinsic remediation demonstration program sponsored by AFCEE is to develop a systematic process for scientifically investigating and documenting natural subsurface attenuation processes that can be factored into overall site remediation plans. The objective of this program and the specific demonstration at IRP Site SS-16 at Langley AFB is to provide solid evidence of intrinsic remediation of dissolved fuel hydrocarbons so that this information can be used to develop an effective groundwater remediation strategy. A secondary goal of this multi-site initiative is to provide a series of regional case studies that demonstrate that natural processes of contaminant

degradation can often reduce contaminant concentrations in groundwater to below acceptable cleanup standards before completion of potential receptor exposure pathways.

Because the objective of this program is to study natural processes in the saturated zone rather than all contaminated media (e.g., soil, soil gas, etc.), technologies have been evaluated based primarily on their potential impact on shallow groundwater and phreatic soils. Significant vadose zone contamination was not identified during this investigation and therefore, technologies that can reduce vadose zone contamination and partitioning of contaminants into groundwater were not evaluated. Additional program objectives set forth by AFCEE include cost effectiveness and minimization of waste. Applicable technologies that may meet these criteria include institutional controls and intrinsic remediation. Soil excavation, slurry walls, sheet piling, groundwater pump and treat, air sparging, carbon adsorption, *ex situ* biological or chemical treatment, and onsite/offsite disposal are not considered attractive technologies for this site.

6.2.2 Contaminant Properties

The site-related contaminants considered as part of this demonstration are the BTEX compounds. The primary source of this contamination is petroleum (fuel oils and other fuels) leaked or spilled during past above ground and underground fuel storage at the site. Residual contamination at the site is present at and below the groundwater table and in the capillary fringe. The physiochemical characteristics of the individual BTEX compounds, which are the most bioavailable, mobile, and toxic of the constituents that make up the released fuel products, will greatly influence the effectiveness and selection of a remedial approach.

The BTEX compounds are generally volatile, highly soluble in water, and adsorb less strongly to soil than other hydrocarbons in a petroleum mixture. These

characteristics allow the BTEX compounds to leach more rapidly from contaminated soil into groundwater, and to migrate as dissolved contamination (Lyman *et al.*, 1992). All of the BTEX compounds are highly amenable to *in situ* degradation by both biotic and abiotic mechanisms.

Benzene is very volatile, with a vapor pressure of 76 millimeters of mercury (mm Hg) at 20°C and a Henry's Law Constant of approximately 0.0054 atmosphere-cubic meters per mole (atm-m³/mol) at 25°C (Hine and Mookerjee, 1975; Jury *et al.*, 1984). The solubility of pure benzene in water at 20°C has been reported to be 1,780 mg/L (Verschueren, 1983). Benzene is normally biodegraded to carbon dioxide, with catechol as a short-lived intermediate (Hopper, 1978; Ribbons and Eaton, 1992).

Toluene is also volatile, with a vapor pressure of 22 mm Hg at 20°C and a Henry's Law Constant of about 0.0067 atm-m³/mol at 25°C (Pankow and Rosen, 1988; Hine and Mookerjee, 1975). Toluene sorbs more readily to soil media relative to benzene, but still is very mobile. The solubility of pure toluene in water at 20°C is approximately 515 mg/L at 20°C (Verschueren, 1983). Toluene has been shown to degrade to pyruvate, caetaldehyde, and completely to carbon dioxide via the intermediate catechol (Hopper, 1978; Wilson *et al.*, 1986; Ribbons and Eaton, 1992).

Ethylbenzene has a vapor pressure of 7 mm Hg at 20°C and a Henry's Law Constant of 0.0066 atm-m³/mol (Pankow and Rosen, 1988; Valsaraj, 1988). Ethylbenzene sorbs more strongly to soils than benzene and toluene (Kenaga and Goring, 1980; Means *et al.*, 1980; Hassett *et al.*, 1983; Fetter, 1993). Pure ethylbenzene is also less soluble than benzene and toluene in water at 152 mg/L at 20°C (Verschueren, 1983; Miller *et al.*, 1985). Ethylbenzene ultimately degrades to carbon dioxide via its intermediate 3-ethylcatechol (Hopper, 1978; Ribbons and Eaton, 1992).

The three isomers of xylene have vapor pressures ranging from 7 to 9 mm Hg at 20°C and Henry's Law Constants of between 0.005 and 0.007 atm-m³/mol at 25°C (Mackay and Wolkoff, 1973; Hine and Mookerjee, 1975; Pankow and Rosen, 1988). A compilation of literature values for sorption coefficients suggests that xylenes sorb to soil with approximately the same strength as ethylbenzene (Wiedemeier *et al.*, 1995). Pure xylenes have water solubilities of 152 to 160 mg/L at 20°C (Bohon and Claussen, 1951; Mackay and Shiu, 1981; Isnard and Lambert, 1988). Xylenes can degrade to carbon dioxide via pyruvate carbonyl intermediates (Hopper, 1978; Ribbons and Eaton, 1992).

On the basis of these physiochemical characteristics, intrinsic remediation, air sparging, biosparging, groundwater extraction, and air stripping technologies all could be effective options for collecting, destroying, and/or treating BTEX contaminants at the site. Some of these options are less desirable, however, after considering site-specific conditions.

6.2.3 Site-Specific Conditions

Three general categories of site-specific characteristics were considered when identifying remedial approaches for comparative evaluation as part of this demonstration. The first category was physical characteristics such as groundwater depth, hydraulic conductivity, gradient, flow direction, and soil type. The second category was the site geochemistry, or how the site contaminants are interacting with electron acceptors, microorganisms, and other site contaminants. Both of these categories influence the types of remedial technologies most appropriate for the site. The third category involved assumptions about future land use and potential receptor exposure pathways. Each of these site-specific characteristics have influenced the development of remedial alternatives included in the comparative evaluation.

6.2.3.1 Physical Characteristics

Site geology and hydrogeology have a profound effect on the transport of contaminants and the effectiveness and scope of required remedial approaches at a given site. Hydraulic conductivity is perhaps the most important aquifer parameter governing groundwater flow and contaminant transport in the subsurface. The velocity of the groundwater and dissolved contamination is directly related to the hydraulic conductivity of the saturated zone. Estimated hydraulic conductivity values from three site wells ranged from 24 to 27 ft/day, characteristic of sand (Freeze and Cherry, 1979).

The observed range of hydraulic conductivities suggests that the shallow water table aquifer is relatively homogeneous (Figures 3.3 and 3.4) meaning that no zones of higher or lower conductivity are apparent. No significant preferential flow paths have been identified; however, the slightly radial groundwater flow pattern (Figure 3.5) tends to distribute dissolved BTEX away from the source area to the southwest (Figure 4.2).

6.2.3.2 Geochemical Characteristics

To satisfy the requirements of indigenous microbial activity and intrinsic remediation, the aquifer also must provide an adequate and available carbon or energy source (e.g., the contamination), electron acceptors, essential nutrients, and proper ranges of pH, temperature, and redox potential. Data collected as part of the field work phase of this demonstration project and described in Sections 3 and 4 of this TS indicate that this site is characterized by adequate and available carbon/energy sources and electron acceptors to support measurable biodegradation of fuel hydrocarbon contamination by indigenous microorganisms. DO, ferric iron, nitrate, sulfate, and carbon dioxide (which is utilized during methanogenesis) represent sources of electron acceptor capacity for the biodegradation of BTEX compounds at the site. The average pH in shallow site

groundwater of 6.6 is within the optimal range for biodegradation of 6 to 8 standard pH units (Wiedemeier *et al.*, 1995). Fuel-hydrocarbon-degrading microorganisms, however, have been known to thrive under a wide range of temperature and pH conditions (Chapelle, 1993). Groundwater data presented in Section 4 strongly support the conclusion that aerobic and anaerobic biodegradation of BTEX is occurring at the site given the current geochemical conditions.

Fuel-hydrocarbon-degrading microorganisms are ubiquitous, and as many as 28 hydrocarbon-degrading isolates (bacteria and fungi) have been discovered in different soil environments (Davies and Westlake, 1979; Jones and Eddington, 1968). Indigenous microorganisms have a distinct advantage over microorganisms injected into the subsurface to enhance biodegradation because indigenous microorganisms are well adapted to the physical and chemical conditions of the subsurface in which they reside (Goldstein *et al.*, 1985). Microbe addition was not considered a viable remedial technology for this site.

6.2.3.3 Potential Exposure Pathways

A pathways analysis identifies the potential human and ecological receptors that could come into contact with site-related contamination and the pathways through which these receptors might be exposed. To have a complete exposure pathway, there must be a source of contamination, a potential mechanism(s) of release, a pathway of transport to an exposure point, an exposure point, and a receptor. If any of these elements do not exist, the exposure pathway is considered incomplete, and receptors will not come into contact with site-related contamination. Evaluation of the potential long-term effectiveness of any remedial technology or remedial alternative as part of this demonstration project includes determining the potential for pathway completion. If a completed exposure pathway exists (e.g., via surface water contact), potential long-term

remedial options may still be sufficient to maintain exposure concentrations below regulatory action levels. Establishing site-specific, risk-based cleanup levels is beyond the scope of this TS.

Assumptions about current and future land uses at a site form the basis for identifying potential receptors, potential exposure pathways, reasonable exposure scenarios, and appropriate remediation goals. USEPA (1991) advises that the land use associated with the highest (most conservative) potential level of exposure and risk that can reasonably be expected to occur should be used to guide the identification of potential exposure pathways and to determine the level to which the site must be remediated.

The contaminant source areas at the site consist of soils above and below the water table containing residual LNAPL beneath the parking lot between Buildings 590 and 596. Access to the parking lot is restricted to Base personnel, workers, and residents. Public access to the site as well as the Base is restricted. Shallow groundwater is expected to serve as the predominant release and transport mechanism. Shallow groundwater at the site flows to the south and southwest and eventually discharges to the Southwest Branch of the Back River. The current downgradient extent of fuel-contaminated groundwater is approximately 300 feet from the river; therefore, discharge of BTEX compounds to this water body does not currently occur.

Although not within the scope of this demonstration, a risk assessment may be required to evaluate potential risks. Under current conditions, the probability for exposure of site contaminants to human receptors is low; however, exposure to Base workers could possibly occur if potential construction activities at the site were to include soil excavation within the source area. No ecological receptors could currently come into contact with fuel hydrocarbon contamination in the shallow groundwater. In summary,

the use of the intrinsic remediation approach at this site will require that access to the source area be restricted and that restrictions on shallow groundwater use be enforced in areas at and downgradient from the site until natural attenuation reduces contaminants to levels that pose no risk. If source reduction technologies such as air sparging, biosparging, or groundwater extraction are implemented, they will have some impact on the short- and long-term land use options, and some level of institutional control and worker protection during remediation will be required.

6.2.3.4 Remediation Goals for Shallow Groundwater

Model results suggest that BTEX compounds in shallow groundwater will naturally attenuate via aerobic and anaerobic biodegradation without further downgradient progression. This means that discharge to nearby surface water bodies is not probable. However, the selected remedial alternative(s) must be able to achieve groundwater concentrations protective of human health and the environment. Although it is unlikely that site groundwater would be ingested by humans, the federal MCL for each of the BTEX compounds is the preliminary RAO for groundwater. The applicable federal MCLs for drinking water are listed in Table 6.1.

TABLE 6.1
GROUNDWATER QUALITY STANDARDS
IRP SITE SS-16
INTRINSIC REMEDIATION TS
LANGLEY AFB, VIRGINIA

Compound	Federal Drinking Water MCL ($\mu\text{g/L}$) ^{a/}
Benzene	5
Toluene	1,000
Ethylbenzene	700
Total Xylenes	10,000

^{a/} USEPA (1994).

This remedial strategy conservatively assumes unrestricted future uses of the shallow groundwater at the site, including a drinking water supply even though there are no current withdrawal points within the boundaries of the Base. Therefore, the preliminary RAO for shallow groundwater within and downgradient of IRP Site SS-16 is reduction of BTEX concentrations in the shallow groundwater to the levels equal to or below the federal MCL for each BTEX compound.

In summary, available data suggest that no groundwater exposure pathways involving human or ecological receptors exist under current conditions. However, future exposure pathways involving human contact and ingestion of the shallow groundwater may be completed unless use of shallow groundwater as a potable or industrial source of water is prohibited by institutional controls within approximately 1,000 feet of the site. In addition, institutional controls should include use of personal protection equipment by intrusive onsite workers (should subsurface construction activities be conducted at the site) to reduce the risk of exposure to BTEX compounds via inhalation and dermal contact. Thus, institutional controls are likely to be a necessary component of any

groundwater remediation strategy for this site. The required duration of these institutional controls may vary depending on the effectiveness of the selected remedial technology at reducing contaminant mass and concentrations in the groundwater.

6.2.4 Summary of Remedial Option Screening and Analysis

Several remedial options have been identified for use in treating the shallow groundwater at the site. Among the initial remedial technologies and approaches considered as part of this demonstration were institutional controls, long-term monitoring, groundwater extraction/containment via vertical wells and/or interceptor trenches; air sparging; physical containment using slurry walls, grout curtains, or sheet piles; funnel and reactive gate walls; and intrinsic remediation. Screening was conducted by considering the program objectives of the AFCEE intrinsic remediation demonstration, physiochemical properties of the BTEX compounds, and other site-specific characteristics such as hydrogeology, geochemistry, land use assumptions, potential exposure pathways, and appropriate remediation goals. All of these factors will influence the technical effectiveness, implementation, and relative cost of options for remediating shallow groundwater underlying and migrating from the site.

Based on the screening process, a single remedial alternative, intrinsic remediation with LTM and institutional controls, was developed for evaluation. Groundwater extraction/containment via vertical wells and/or interceptor trenches was eliminated due to high operation and maintenance (O&M) costs and well-known ineffectiveness in achieving remedial objectives. Physical containment was eliminated due to high installation costs and limited service life. The screening process provided sufficient support to select the optimal remedial alternative, and thus a detailed comparative analysis was unnecessary.

6.3 DESCRIPTION OF THE SELECTED REMEDIAL ALTERNATIVE - INTRINSIC REMEDIATION AND INSTITUTIONAL CONTROLS WITH LONG-TERM GROUNDWATER MONITORING

Intrinsic remediation is achieved when natural attenuation mechanisms bring about a reduction in the total mass of a contaminant in the soil or dissolved in groundwater. Intrinsic remediation results from the integration of several subsurface attenuation mechanisms that are classified as either destructive or nondestructive. Destructive attenuation mechanisms include biodegradation, abiotic oxidation, and hydrolysis. Nondestructive attenuation mechanisms include sorption, dilution (caused by dispersion and infiltration), and volatilization. In some cases, intrinsic remediation will reduce dissolved contaminant concentrations below numerical concentration goals intended to be protective of human health and the environment. As indicated by the evidence of intrinsic remediation described in Section 4, these processes are occurring at IRP Site SS-16 and will continue to reduce contaminant mass in the plume area.

Model GSW is intended to predict the fate and transport of dissolved BTEX compounds if engineered remedial action is not implemented at the site. To accomplish this, the model assumes a gradually weathering source of BTEX in the shallow aquifer. Results suggest that the dissolved BTEX plume will decrease in extent and concentration over time. The model predicts that the BTEX plume will be reduced to concentrations below 5 µg/L within approximately 50 years.

Implementation of intrinsic remediation at Site SS-16 would require the use of institutional controls such as land use restrictions and well permit regulation. Land use restrictions may include placing long-term restrictions on excavation/drilling activities (to ensure proper worker protection from the site contaminants) and on construction of recreational facilities (i.e., playgrounds or picnic areas) within the site vicinity. Long-term restrictions on groundwater well installations within and downgradient from the

plume area also would be required. The intent of these restrictions would be to reduce the potential for receptor exposure to contaminants by legally restricting activities within areas affected by site-related contamination.

LTM would be conducted every second year as part of this remedial approach to evaluate the progress of natural attenuation processes. LTM includes two types of monitoring wells. LTM wells are intended to determine if the behavior of the plume is changing and to monitor the progress of BTEX reduction at the site. POC wells are intended to detect movements of the plume outside the negotiated perimeter of containment, and to trigger an action to manage the risk associated with such expansion if the BTEX concentrations at these wells exceed the federal groundwater MCLs listed in Table 6.1.

As a part of LTM, groundwater monitoring would be performed at 14 wells. The wells would be chosen to monitor the main contaminant plume within the parking lot between Buildings 590 and 596. Wells would be used to monitor groundwater at the water table and approximately 15 feet below the water table to monitor the vertical distribution of BTEX in the plume area. Additional details (including monitoring locations) for LTM of groundwater are provided in Section 7. If implementation of the remedial alternative does not result in a decrease in dissolved contaminant concentrations, additional corrective action may be necessary, and land use restrictions would require reevaluation.

Public education on the selected alternative would be developed to inform Base personnel and residents of the scientific principles underlying intrinsic remediation. This education could be accomplished through debriefings, presentations, and posting of signs where appropriate. Periodic site reviews could also be conducted every other year using data collected from the long-term groundwater monitoring program. The purpose of

these periodic reviews would be to evaluate the extent of contamination, assess contaminant migration and attenuation through time, document the effectiveness of institutional controls at the site, and reevaluate the need for additional remedial actions at the site.

6.4 EVALUATION OF THE SELECTED REMEDIAL ALTERNATIVE - INTRINSIC REMEDIATION AND INSTITUTIONAL CONTROLS WITH LONG-TERM GROUNDWATER AND SURFACE WATER MONITORING

6.4.1 Effectiveness

Section 5 of this document presents the results of the Bioplume II modeling of intrinsic remediation at IRP Site SS-16. Model GSW assumes that site remediation relies entirely on natural attenuation mechanisms. Results of the model suggest that 100 percent of the dissolved BTEX will be removed from the groundwater system through intrinsic remediation. Model results suggest that after 50 years, the dissolved BTEX concentrations may be less than 5 µg/L. Based on the model results and evidence of significant aerobic and anaerobic biodegradation in the shallow groundwater (Section 4), intrinsic remediation is an effective method to complete the restoration of site groundwater.

The effectiveness of this remedial alternative requires that excavations or drilling within the source area be conducted only by properly protected site workers. Long-term land use restrictions would be required to ensure that shallow groundwater is not pumped or removed for potable use within a radius of approximately 1,000 feet from the margins of the existing BTEX plumes. Existing health and safety plans should be enforced to reduce risks to onsite workers during additional excavation or from installing and monitoring additional wells.

Compliance with program goals is one component of the long-term effectiveness evaluation criterion. This alternative would satisfy program objectives designed to promote intrinsic remediation as a component of site remediation and to scientifically document natural processes. This alternative also satisfies program goals for cost effectiveness and waste minimization.

The intrinsic remediation approach is based on the effectiveness of natural processes that minimize contaminant migration and reduce contaminant mass over time, and the effectiveness of institutional controls. As described earlier, model results indicate that the BTEX plume will be contained and reduced within the source area via aerobic and anaerobic biodegradation. Therefore, the effectiveness of intrinsic remediation with LTM and long-term institutional controls is favorable.

6.4.2 Implementability

The intrinsic remediation approach with LTM is not technically difficult to implement. Installation of LTM wells and monitoring of groundwater are standard procedures. Long-term management efforts would be required to ensure proper sampling procedures are followed. Periodic site reviews should be conducted to confirm the adequacy and completeness of LTM data and to verify the effectiveness of this remediation approach. There may also be administrative concerns associated with long-term enforcement of groundwater use restrictions. Future land use within the source area may be impacted by leaving contaminated soil and groundwater in place. Regulators would have to be informed of the benefits and limitations of the intrinsic remediation option. Educational programs for Base personnel and residents are not difficult to implement. Where the effectiveness of this option has been supported, the initial regulatory reaction to this alternative has been positive.

6.4.3 Cost

The cost of intrinsic remediation with LTM is summarized in Table 6.2. Capital costs are limited to the construction of 9 new monitoring wells. Included in the \$322,000 total present worth cost estimate are the costs of maintaining institutional controls and long-term groundwater monitoring for a total of 50 years.

TABLE 6.2
INTRINSIC REMEDIATION WITH LTM - COST ESTIMATE
 IRP SITE SS-16
 INTRINSIC REMEDIATION TS
 LANGLEY AFB, VIRGINIA

<u>Capital Costs</u>	<u>Cost</u>
Design/Construct 9 LTM Wells	\$22,200
<u>Monitoring Costs (per Sampling Event)</u>	<u>Cost per Event</u>
Conduct Groundwater Sampling at 11 wells (per event) (every second year for first 20 years followed by every fifth year)	\$14,400
Maintain Institutional Controls/Public Education (50 years)	\$5,000
Project Management and Reporting (every second year for first 20 years followed by every fifth year)	\$11,100
<u>Present Worth of Alternative ^{a/}</u>	<u>\$322,000</u>

^{a/} Based on an annual adjustment factor of 7 percent (USEPA, 1993).

SECTION 7

LONG-TERM MONITORING PLAN

7.1 OVERVIEW

At IRP Site SS-16, LTM is a required component of the selected remedial alternative discussed in Section 6; therefore, a long-term groundwater monitoring plan must be developed. The purpose of the LTM component of the selected remedial alternative is to assess site conditions over time, verify model results, confirm the effectiveness of the remedial alternative, assess compliance with regulatory cleanup goals, and evaluate the need for additional remediation. The LTM plan consists of identifying groundwater sampling locations and developing a sampling and analysis strategy to demonstrate attainment with site-specific remediation goals. The strategy described in this section is designed to assess the effectiveness of the remedial alternative through measurement of the reduction of contaminant mass, and the rate of groundwater remediation. In the event that data collected under this LTM program indicate that the implemented remedial alternative is insufficient to achieve regulatory levels, considered to be protective of human health and the environment, at the POC wells, additional engineered controls to augment the beneficial effects of intrinsic remediation may be necessary.

7.2 LONG-TERM GROUNDWATER MONITORING WELLS

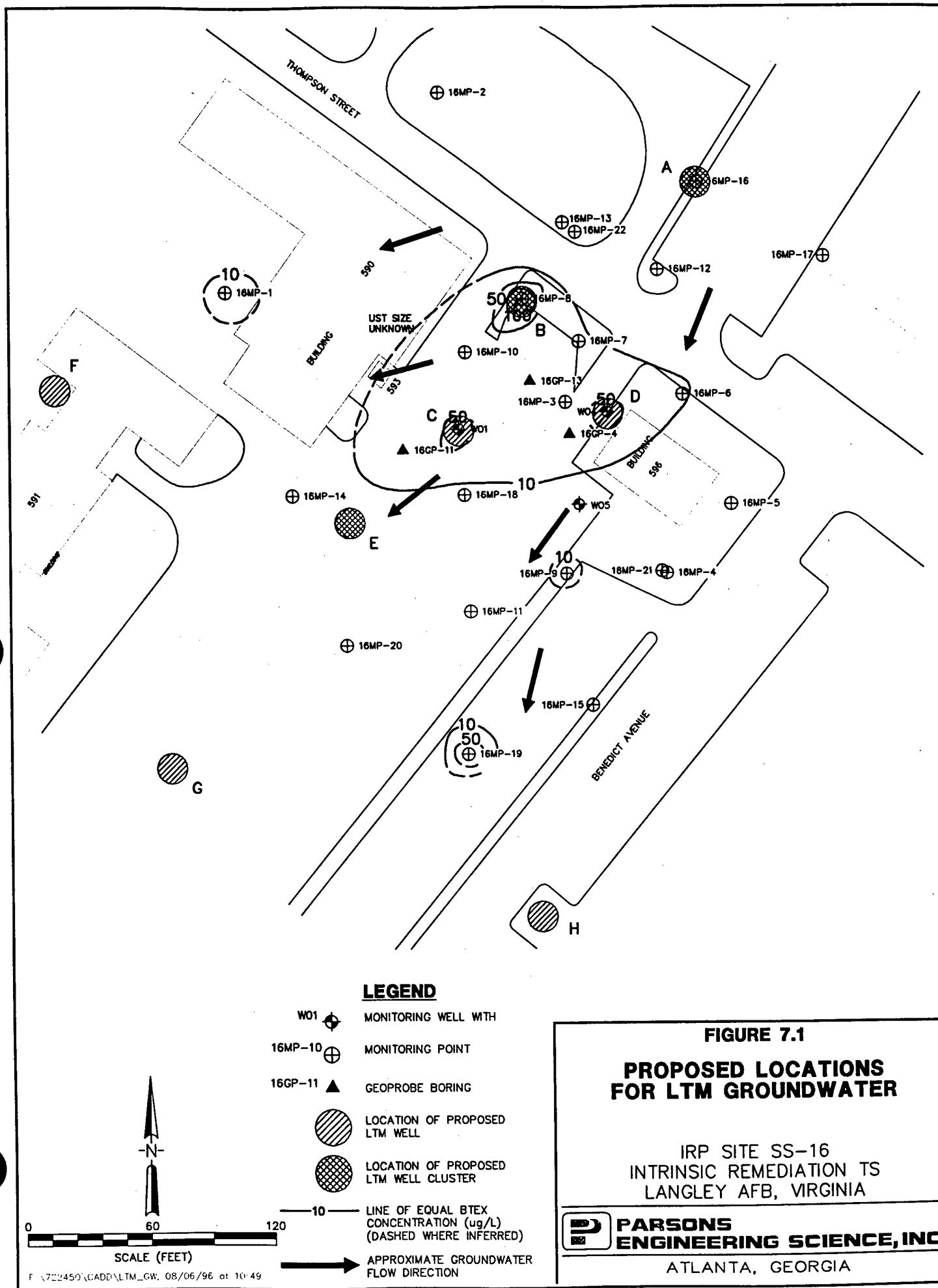
A total of 11 monitoring wells will be utilized at the site as part of LTM. Of these wells, two exist and the remaining 9 require installation. Six of the 11 wells will be installed in three clusters of two wells. Each cluster will include a shallow well screened across the water table and a well installed to approximately 25 feet bgs to monitor the

vertical distribution of BTEX in the shallow aquifer. The remaining three wells to be installed will be screen across the water table. Proposed LTM well locations (labeled A through H) are shown in Figure 7.1. Proposed shallow LTM wells will be constructed with 10-foot screens. The shallow well in each cluster will be screened across the water table with approximately 8 feet of screen installed below the water table; the deep well in each cluster will be screened in deeper saturated sands with a 5-foot screen extending from 20 to 25 feet bgs.

Monitoring well location A is located upgradient from the plume and source area. Monitoring well locations B through E are located within the BTEX plume. Monitoring well locations F through H, which will serve as POC wells, are located downgradient from the source area and within the downgradient fringe of the BTEX plume. Well locations, selected to evaluate contamination within and around the plume, are as follows:

- Location A -- background;
- Location B -- anaerobic treatment zone;
- Location C -- area of benzene concentrations greater than federal MCL/anaerobic zone (existing monitoring well W01);
- Location D -- area of benzene concentrations greater than federal MCL/anaerobic zone (existing monitoring well W04);
- Location E -- aerobic treatment zone; and
- Locations F through H -- POC wells.

POC monitoring well locations F through H are located beyond the downgradient fringe of the BTEX plume.



7.3 GROUNDWATER SAMPLING

To ensure that sufficient contaminant removal is occurring to meet site-specific RAOs, the long-term groundwater monitoring plan includes a SAP. Groundwater samples will be collected and analyzed annually from LTM wells to verify that naturally occurring processes are effectively reducing contaminant mass and mobility. Reductions in toxicity will be implied by mass reduction.

7.3.1 Sampling Frequency

Each of the LTM and POC wells will be sampled every second year for 20 years, then every fifth year for the following 30 years. If the data collected during this time period support the effectiveness of the selected remedial alternative at this site, it may be possible to reduce or eliminate sampling. If the data collected at any time during the monitoring period indicate the need for additional remedial activities at the site, sampling frequency should be adjusted accordingly.

7.3.2 Analytical Protocol

All LTM and POC wells in the LTM program will be sampled and analyzed to determine compliance with chemical-specific remediation goals and to verify the effectiveness of naturally-occurring remediation processes at the site. At the beginning of each annual sampling event, water levels will be measured at all site monitoring wells. Groundwater samples collected from the LTM and POC wells will be analyzed for the parameters listed in Table 7.1. A site-specific groundwater SAP should be prepared prior to initiating the LTM program.

TABLE 7.1
LONG-TERM MONITORING ANALYTICAL PROTOCOL FOR GROUNDWATER
 IRP SITE SS-16
 INTRINSIC REMEDIATION TS
 LANGLEY AFB, VIRGINIA

Analysis	Method/Reference	Comments	Data Use	Recommended Frequency of Analysis	Sample Volume, Sample Container, Sample Preservation	Field or Fixed-Base Laboratory
Ferrous (Fe^{+2})	Colorimetric A3500-Fe D	Field only	May indicate an anaerobic degradation process due to depletion of oxygen, nitrate, and manganese	Every second year for 20 years, then every fifth year for 30 years.	Collect 100 mL of water in a glass container; acidify with hydrochloric acid per method	Field
Ferrous (Fe^{+2})	Colorimetric Hach 25140-25	Alternate method; field only	Same as above	Every second year for 20 years, then every fifth year for 30 years.	Collect 100 mL of water in a glass container	Field
Temperature	E170.1	Field only	Metabolism rates for microorganisms depend on temperature	Every second year for 20 years, then every fifth year for 30 years.	N/A	Field
Dissolved Oxygen	Dissolved oxygen meter	Refer to method A4500 for a comparable laboratory procedure	The oxygen concentration is a data input to the Bioplume model; concentrations less than 1 mg/L generally indicate an anaerobic pathway	Every second year for 20 years, then every fifth year for 30 years.	Collect 300 mL of water in biochemical oxygen demand bottles; analyze immediately; alternately, measure dissolved oxygen <i>in situ</i>	Field
pH	E150.1/SW9040, direct reading meter	Protocols/Handbook methods	Aerobic and anaerobic processes are pH-sensitive	Every second year for 20 years, then every fifth year for 30 years.	Collect 100–250 mL of water in a glass or plastic container; analyze immediately	Field
Conductivity	E120.1/SW9050, direct reading meter	Protocols/Handbook methods	General water quality parameter used as a marker to verify that site samples are obtained from the same groundwater system	Every second year for 20 years, then every fifth year for 30 years.	Collect 100–250 mL of water in a glass or plastic container	Field
Nitrate (NO_3^{-1})	IC method E300 or method SW9056; colorimetric, method E353.2	Method E300 is a Handbook method; method SW9056 is an equivalent procedure	Substrate for microbial respiration if oxygen is depleted	Every second year for 20 years, then every fifth year for 30 years.	Collect up to 40 mL of water in a glass or plastic container; cool to 4°C; analyze within 48 hours	Fixed-base

TABLE 7.1 (Continued)
LONG-TERM MONITORING ANALYTICAL PROTOCOL FOR GROUNDWATER
 IRP SITE SS-16
 INTRINSIC REMEDIATION TS
 LANGLEY AFB, VIRGINIA

Analysis	Method/Reference	Comments	Data Use	Recommended Frequency of Analysis	Sample Volume, Sample Container, Sample Preservation	Field or Fixed-Base Laboratory
Sulfate (SO_4^{2-})	IC method E300 or method SW9056 or Hach Sulfa Ver 4 method	Method E300 is a Handbook method; method SW9056 is an equivalent procedure. Hach method is Photometric.	Substrate for anaerobic microbial respiration	Every second year for 20 years, then every fifth year for 30 years.	Collect up to 40 mL of water in a glass or plastic container; cool to 4°C	Fixed-base or field (for Hach method)
Redox potential	A2580 B	Measurements are made with electrodes; results are displayed on a meter; samples should be protected from exposure to atmospheric oxygen	The redox potential of groundwater influences and is influenced by the nature of the biologically mediated degradation of contaminants; the redox potential of groundwater may range from more than 200 mV to less than -400 mV	Every second year for 20 years, then every fifth year for 30 years.	Collect 100-250 mL of water in a glass container, filling container from bottom; analyze immediately	Field
Methane; carbon dioxide	RSKSOP-114 modified to analyze water samples for methane and carbon dioxide by headspace sampling with dual thermal conductivity and flame ionization detection	Method published and used by the U.S. Environmental Protection Agency (EPA) Robert S. Kerr Laboratory	The presence of methane suggests BTEX degradation via an anaerobic pathway utilizing carbon dioxide (carbonate) as the electron acceptor (methanogenesis)	Every second year for 20 years, then every fifth year for 30 years.	Collect water samples in 40 mL volatile organic analysis (VOA) vials with butyl gray/Teflon-lined caps; cool to 4°C	Fixed-base
Aromatic hydrocarbons (BTEX)	Purge and trap GC method SW8020	Handbook method; analysis may be extended to higher molecular weight alkyl benzenes	BTEX, are the primary target analyte for monitoring natural attenuation; BTEX concentrations must also be measured for regulatory compliance	Every second year for 20 years, then every fifth year for 30 years.	Collect water samples in a 40 mL VOA vial; cool to 4°C; add hydrochloric acid to pH 2	Fixed-base

NOTES:

1. "Hach" refers to the Hach Company catalog, 1990.
2. "A" refers to *Standard Methods for the Examination of Water and Wastewater*, 18th edition, 1992.
3. "E" refers to *Methods for Chemical Analysis of Water and Wastes*, (USEPA, 1979).
4. "Protocols" refers to the AFCEE (1992) *Environmental Chemistry Function Installation Restoration Program Analytical Protocols*.
5. "Handbook" refers to the AFCEE (1993) *Handbook to Support the Installation Restoration Program (IRP) Remedial Investigations and Feasibility Studies (RI/FS)*.
6. "SW" refers to the *Test Methods for Evaluating Solid Waste, Physical, and Chemical Methods*, SW-846, 3rd edition (USEPA, 1986).
7. "ASTM" refers to the *American Society for Testing and Materials Methods*, current edition.
8. "RSKSOP" refers to Robert S. Kerr (USEPA NRMRL) *Standard Operating Procedure*.
9. "LUFT" refers to the State of California (1988) *Leaking Underground Fuel Tank Field Manual*.
10. *International Journal of Environmental Analytical Chemistry*, Volume 36, pp. 249-257, "Dissolved Oxygen and Methane in Water by a Gas Chromatography Headspace Equilibration Technique," (Kampbell et al.)

SECTION 8

CONCLUSIONS AND RECOMMENDATIONS

This report presents the results of a TS conducted to evaluate the use of intrinsic remediation for remediation of fuel-hydrocarbon-contaminated groundwater in the vicinity of the IRP Site SS-16 at Langley AFB, Virginia. Specifically, the finite-difference groundwater model Bioplume II was used in conjunction with site-specific geologic, hydrologic, and laboratory analytical data to simulate the migration and biodegradation of fuel hydrocarbon compounds dissolved in groundwater. To collect the data necessary for the intrinsic remediation demonstration, Parsons ES researchers collected soil and groundwater samples from the site. Physical and chemical data collected under this program were supplemented (where necessary) with data collected during previous site characterization events.

Comparison of BTEX, electron acceptor, and biodegradation byproduct isopleth maps for the IRP Site SS-16 provides strong qualitative evidence of biodegradation of BTEX compounds (Section 4). Geochemical data strongly suggest that biodegradation of fuel hydrocarbons is occurring at the site via aerobic processes and the anaerobic processes of iron reduction, nitrate reduction, sulfate reduction, and methanogenesis. Patterns observed in the distribution of hydrocarbons, electron acceptors, and biodegradation byproducts further indicate that biodegradation is reducing dissolved BTEX concentrations in site groundwater.

Site-specific geologic, hydrologic, and laboratory analytical data then were used in the Bioplume II numerical groundwater model to simulate the effects of advection, dispersion,

sorption, contaminant loading, and biodegradation on the fate and transport of the dissolved BTEX plume (Section 5). Extensive site-specific data were used for model calibration and implementation. Model parameters that could not be obtained from existing site data were estimated using widely accepted literature values for soils similar to those found at the site. Conservative aquifer parameters were used to construct the Bioplume II model for this study, and therefore, the model results presented herein represent worst-case scenarios.

For simulation model GSW, it was assumed that natural physical weathering of the source areas would persist for the duration of the simulation. This scenario suggests that approximately 100 percent of the BTEX mass dissolving into the groundwater will be removed by intrinsic bioremediation with dissolved BTEX concentrations approaching less than 5 µg/L in approximately 50 years.

The results of this study suggest that intrinsic remediation of BTEX compounds is occurring at the site, and intrinsic remediation should ensure protection of human health and the environment. Therefore, the Air Force recommends that intrinsic remediation with LTM and institutional controls be implemented at the site. Institutional controls such as restrictions on shallow groundwater use and protective equipment for workers during future drilling or excavation activities should prevent completion of pathways while site remediation is in progress.

To verify the results of the Bioplume II modeling effort, and to ensure that the selected remediation is progressing at rates sufficient to meet objectives, groundwater from 11 LTM and POC wells should be sampled and analyzed for the parameters listed in Table 7.1. Figure 7.1 shows suggested locations for the LTM and POC wells. These locations should be sampled every second year for 20 years, and then sampled every fifth year for the following 30 years. At this time, sampling will cease, decrease in frequency, or will

continue annually as dictated by the analytical results. If data collected under this LTM program indicate that the implemented remedial alternative is insufficient to reduce BTEX concentrations to regulatory levels considered protective of human health and the environment, additional engineered controls to augment the beneficial effects of intrinsic remediation would be necessary.

SECTION 9

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