ASSESSMENT OF INTRINSIC BIOREMEDIATION OF GASOLINE CONTAMINATION IN THE SHALLOW AQUIFER, LAUREL BAY EXCHANGE, MARINE CORPS AIR STATION BEAUFORT, SOUTH CAROLINA

By James E. Landmeyer, Francis H. Chapelle, and Paul M. Bradley

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CONVERSION FACTORS, VERTICAL DATUM, AND ABBREVIATIONS

Multiply	By	To Obtain
	Length	
inch (in.)	25.4	millimeter
foot (ft)	0.3048	meter
foot per foot (ft/ft)	0.3048	meter per meter
mile (mi)	1.609	kilometer
	Area	
square mile (mi^2)	2.590	square kilometer
	Flow	
foot per day (ft/d)	0.3048	meter per day
foot per year (ft/yr)	0.3048	meter per year
	Volume	
gallon (gal)	3.785	liter

Temperature: In this report, temperature is given in degrees Celsius (°C), which can be converted to degrees Fahrenheit (°F) by the following equation:

$$°F = (1.8 \times °C) + 32$$

Sea Level: In this report, "sea level" refers to the National Geodetic Vertical Datum of 1929--a geodetic datum derived from a general adjustment of the first-order level nets of the United States and Canada, formerly called Sea Level Datum of 1929.

Chemical concentration: In this report, chemical concentration in water is expressed in metric units as milligrams per liter (mg/L) or micrograms per liter (μg/L).

Radiochemical activity: In this report, radioactivity units are given in microcuries (μCi).

CONVERSION FACTORS, VERTICAL DATUM, AND ABBREVIATIONS--Continued

Biodegradation rate constant: In this report, first-order kinetics are used to model biodegradation rates of petroleum hydrocarbons. First-order rate constants (K_{bio}) are expressed in units of percent of compound degraded per day (pct/d). Because percent is dimensionless, this reduces to units of inverse days (d^{-1}).

Adsorption coefficient: In this report, the adsorption coefficient (K_{ad}) is expressed as feet cubed per milligram (ft^3/mg), which are equivalent to units of liters per kilogram (L/kg).

Any use of trade, product, or firm names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

Other units used in report:

gram = g
micrograms = µg
micrometer = µm
milliliter = mL
parts per million = ppm

Abbreviations used in this report:

BTEX	- benzene, toluene, ethylbenzene, and total xylenes
DIC	- dissolved inorganic carbon
FID	- flame-ionization detection
GC	- gas chromatography
MCAS	- Marine Corps Air Station
MCL	- maximum contaminant level
MSGL	- Microbial Studies Group Laboratory
MTBE	- methyl-tert-butyl-ether
POC	- point(s) of contact
SCDHEC	- South Carolina Department of Health and Environmental Control
SUTRA	- **S**aturated - **U**nsaturated **TRA**nsport
TEAP	- terminal electron-accepting process
USGS	- U.S. Geological Survey

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ABSTRACT

Laboratory, field, and digital solute-transport-modeling studies demonstrate that microorganisms indigenous to the shallow ground-water system at Laurel Bay Exchange, Marine Corps Air Station Beaufort, South Carolina, can degrade petroleum hydrocarbons in gasoline released at the site. Microorganisms in aquifer sediments incubated in the laboratory under aerobic and anaerobic conditions mineralized radiolabeled carbon 14-toluene to ^{14}C-carbon dioxide with first-order rate constants of $K_{bio} = -0.640$ per day and $K_{bio} = -0.003$ per day, respectively. Digital solute-transport modeling using the numerical code SUTRA revealed that anaerobic biodegradation of benzene occurs with a first-order rate constant near $K_{bio} = -0.00025$ per day. Sandy aquifer material beneath Laurel Bay Exchange is characterized by relatively high hydraulic conductivities ($K_{aq} = 8.9$ to 17.3 feet per day), average ground-water flow rate of about 60 feet per year, and a relatively uniform hydraulic gradient of 0.004 feet per foot. The sandy aquifer material also has low adsorptive potentials for toluene and benzene (both about $K_{ad} = 2.0 \times 10^{-9}$ cubic feet per milligram), because of the lack of natural organic matter in the aquifer. The combination of this ground-water-flow rate and absence of significant adsorptive capacity in the aquifer permits toluene and benzene concentrations to be detected downgradient from the source area in monitoring wells, even though biodegradation of these compounds has been demonstrated. Solute-transport simulations, however, indicate that toluene and benzene will not reach the Broad River, the nearest point of contact with wildlife or human populations, about 3,600 feet west of the site boundary. These simulations also show that contamination will not be transported to the nearest Marine Corps property line about 2,400 feet south of the site. This is primarily because the source of contaminants has essentially been removed, and the low adsorptive capacity of the aquifer sediments has prevented the occurrence of an adsorbed, continuous source of petroleum hydrocarbons. Therefore, digital simulations of toluene and benzene transport at Laurel Bay Exchange indicate that intrinsic bioremediation could be a successful remediation alternative for prohibiting transport of dissolved toluene and benzene to the Broad River.

INTRODUCTION

An unknown volume of gasoline from the underground storage tank system at the Laurel Bay Exchange, Marine Corps Air Station (MCAS) Beaufort, S.C., was detected in the subsurface in September 1991. A contamination assessment made during March and April 1993 indicated that petroleum hydrocarbon concentrations in soils and ground water exceeded maximum contaminant levels (MCL's) for ground water established by the South Carolina Department of Health and Environmental Control (SCDHEC) (U.S. Navy Department, 1993). Recommendations were made to reduce these concentrations to compliable levels and included (1) tank excavation (source removal) and thermal treatment (incineration) of the removed soil, (2) ground-water extraction and reinjection, and (3) enhancement of naturally occurring biodegradation through engineering processes at the site (U.S. Navy Department, 1993). The tanks and surrounding sediments were excavated and removed in 1992 pursuant to SCDHEC regulations (F. Araico, Marine Corps Air Station Beaufort, written commun., 1994).

The U.S. Geological Survey (USGS), in cooperation with the Southern Division, Naval Facilities Engineering Command, U.S. Navy, and MCAS Beaufort quantified hydrologic, geochemical, and microbial data in sediments from Laurel Bay Exchange to determine if contaminant transport will occur to pre-defined points-of-contact (POC) such as adjacent surface-water bodies. The objective of this study is to establish a framework for assessing intrinsic bioremediation or a remedial alternative consistent with recent guidance documents prepared by the SCDHEC.

Purpose and Scope

The results presented in this report summarize a laboratory-, field-, and numerical-modeling-based study focused on the assessment of intrinsic bioremediation of gasoline in the shallow aquifer at Laurel Bay Exchange, MCAS Beaufort, S.C. (hereafter referred to as either Laurel Bay or the site). This study provides the necessary criteria to support intrinsic bioremediation as a feasible remedial strategy compared to the more costly, engineered alternatives offered in the Navy's original assessment report. This study consisted of (1) delineating the 1994 location of two different hydrocarbon plumes at the site (benzene, toluene, ethylbenzene, and total xylenes--BTEX, and the gasoline additive methyl-tert-butyl-ether --MTBE); (2) assessing the hydrologic conditions in the shallow aquifer system, and identifying potential points of ground-water discharge that coincide with points-of-contact (POC) or MCAS property boundaries; (3) determining the rate of toluene degradation under aerobic and anaerobic aquifer conditions using radiolabeled toluene, and the degree of toluene adsorption onto aquifer sediments; (4) using a digital solute-transport model to estimate the anaerobic degradation rate of benzene, and a laboratory study to assess the degree of benzene adsorption onto aquifer sediments; and (5) conducting a digital solute-transport analysis designed to estimate rates of toluene and benzene transport in the aquifer in order to estimate the extent of toluene and benzene transport to delineated POC or property lines by incorporating data gathered in steps 1-4.

Description of Study Area

The Laurel Bay Exchange, MCAS, in Beaufort, S.C., is located on Port Royal Island, in the Sea Islands of the Atlantic Coastal Plain physiographic province (fig. 1). The service station at the site handled gasoline that leaked from underground storage tanks into the silty sand sediments that comprise the Pleistocene to Holocene surficial terrace deposits on Port Royal Island. The surface sediments at the site, to a depth of around 40 ft, consist of Holocene (<7,000 years Before Present) fine-grained sand and represent a back-barrier island depositional facies. The lithology of these sediments is shown in a representative lithologic log of a boring near LB-EX-14 (fig. 2). The uncontaminated sediments at the site are comprised of fine-to-coarse grained sands and some silt coated with ferric oxyhydroxides. This indicates the relatively shallow depth of the ground water and its saturation with dissolved oxygen. The amount of ferric oxyhydroxide coating diminishes, however, as depth and petroleum hydrocarbon concentrations increase.

Framework for Assessing Intrinsic Bioremediation

The efficiency of intrinsic bioremediation to limit contaminant migration in ground-water systems can be assessed by quantitatively comparing rates of contaminant transport to rates of biodegradation. If rates of transport by ground water are fast relative to rates of biodegradation, then contaminants may migrate with ground water and potentially reach POC with human or wildlife populations. Conversely, if transport rates are slow relative to biodegradation rates, contaminant migration will be more confined and be less likely to reach POC. In either case, the efficiency of intrinsic bioremediation can be assessed at a particular site by evaluating the presence or absence of contaminant transport to pre-determined POC. Thus, this assessment includes determining the hydrologic (rates of ground-water flow), geochemical (adsorption properties of the aquifer material), microbial (rates of degradation), and demographic (POC) constraints in the system.

The U.S. Geological Survey (USGS), in cooperation with the Southern Division, Naval Facilities Engineering Command, U.S. Navy, and MCAS Beaufort, has developed a framework for assessing the efficiency of intrinsic bioremediation that is based on these components. In this framework, hydrologic, geochemical, and microbial data are integrated using a digital solute-transport model to determine rates of contaminant transport from a source area to pre-defined POC such as adjacent surface-water bodies. This framework is consistent with recent guidance documents prepared by the SCDHEC and is designed for application at sites where ground-water contamination is the principle issue of concern.

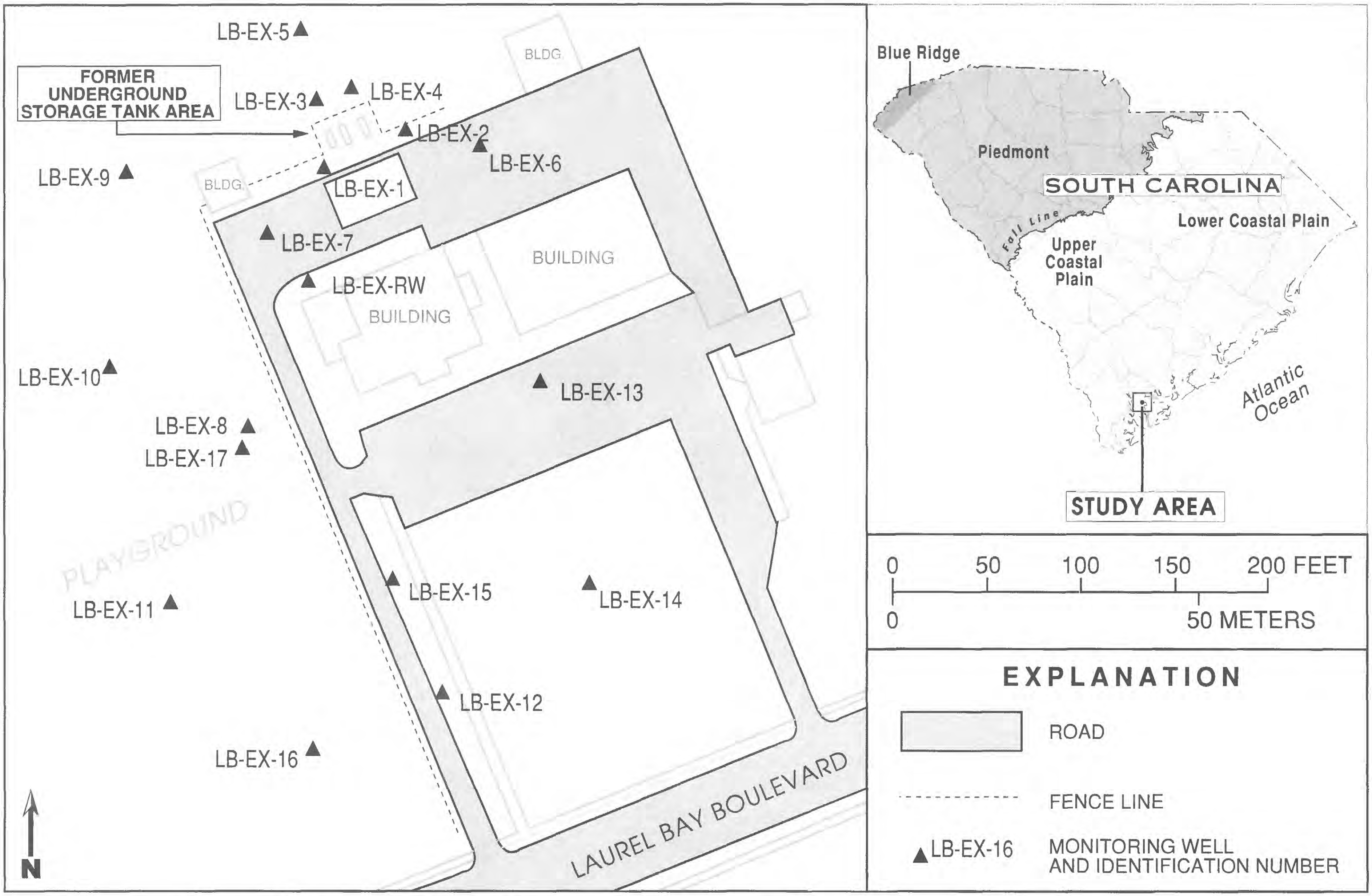

Figure 1. Location of Laurel Bay Exchange, Marine Corps Air Station Beaufort, S.C., study area.

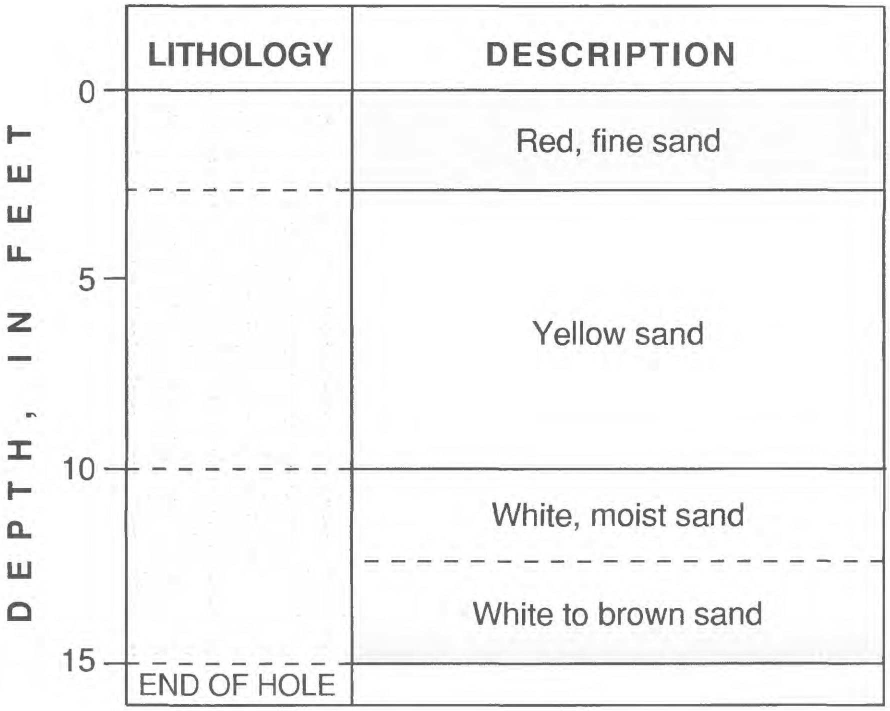

Figure 2. Lithologic description from a borehole located near LB-EX-14.

FIELD AND LABORATORY DATA-COLLECTION METHODS

Ground-water samples were collected and analyzed for BTEX and MTBE concentrations to document the 1994 extent of petroleum hydrocarbons in ground water at the Laurel Bay site. Laboratory experiments were performed to determine the capacity of the aquifer material to adsorb toluene and benzene, and to estimate rates of toluene degradation, whereas benzene degradation was determined using an iterative digital solute-transport modeling approach. Hydrologic, geochemical, and microbial values were evaluated within a framework based on digital solute-transport modeling to determine contaminant transport relative to containment at Laurel Bay.

Field Sample Collection and Analysis

Sampling of existing monitoring wells at the site for water-chemistry data, BTEX and MTBE concentrations, and aquifer sediment samples for laboratory degradation experiments was conducted on March 10 and 11, 1994. An initial trip to the site was made on February 10, 1994, to collect aquifer sediments for laboratory determination of adsorption coefficients (K_{ad}) for toluene and benzene. A synoptic water-level measurement was made on all existing monitoring wells on March 10, 1994, using a steel tape. All water levels were corrected to sea level.

During well purging, measurements of water temperature (in degrees Celsius) and pH (in standard units) were made until stable values were obtained. Dissolved-oxygen concentrations were quantified using the Winkler titration method (Hach Company, 1989). Dissolved ferrous iron [Fe(II)], and sulfide concentrations were determined using the Hach colorimetric method (Stookey, 1970). Ground-water samples to be analyzed for water-chemistry data and BTEX and MTBE concentrations were collected following the purging of the standing-well volume using a peristaltic pump (about 5 gallons, equivalent to 3 well volumes). Ground-water samples to be analyzed for BTEX and MTBE concentrations were collected in a Teflon bailer, transferred to 40 mL, pre-preserved (with HCl) amber glass vials using a bottom-discharge stopcock on the bailer, sealed with Teflon-lined septa screw-caps, and placed on ice. All water samples were collected in duplicate for each well sampled, and were delivered to a contract, SCDHEC-certified laboratory (#40111) within 3 days of sample collection. Samples for dissolved inorganic carbon (DIC), an indicator of hydrocarbon degradation, and methane (CH_4) analyses were collected in the field by passing 5 mL of ground water through a 0.45-µm filter attached to a 10-mL syringe into separate, sealed vials. Methane and DIC concentrations were quantified in the USGS Microbial Studies Group Laboratory (MSGL) by flame ionization detection (FID) gas chromatography (GC). Samples for inorganic cation and anion analyses in ground water were collected in polyethylene bottles after filtration with a 0.45-micron filter. All anions were quantified in the USGS MSGL by ion-conductivity detection. Contaminated aquifer sediment was collected near LB-EX-8 (fig. 1) using an alcohol-rinsed, stainless-steel hand auger, and placed in pre-sterilized, wide-mouthed glass mason jars. These jars were stored on ice in the field and in the refrigerator in the MSGL until analysis.

Laboratory Experiments

The primary processes that can affect the migration of organic hydrocarbon contaminants from a source area in the subsurface are adsorption and microbial degradation. Both processes were quantified in the USGS MSGL. The extent to which these factors interact to affect contaminant migration are then examined in a framework using a predictive digital solute-transport and ground-water-flow model.

Adsorption coefficients for toluene and benzene for aquifer sediments from the site were determined using a modification of the method described in Schwarzenbach and Westall (1981). Approximately 5 g of dried, sterilized (to avoid potential microbial degradation affects) aquifer sediment collected near LB-EX-14 (fig. 1) was placed in septated serum vials, and amended with solutions of either 0, 5, 10, and 50 µg of toluene dissolved in a solution of ground water and MTBE to represent *in situ* conditions. All vials were equilibrated by shaking on a vibrating table for 1 hour. Samples of the liquid fraction were analyzed for toluene using FID with GC. The amount of compound adsorbed to aquifer material was the difference between the amount added and the amount present in the liquid fraction after equilibration. Concentrations of the toluene measured were regressed against concentrations of toluene added to obtain a linear adsorption coefficient. The same procedure was used to determine the adsorption coefficient for benzene onto aquifer sediments from the Laurel Bay site.

The microbial degradation of toluene was determined by quantifying the rate of production of radiolabeled $^{14}CO_2$ from a known amount of radiolabeled toluene added to a microcosm containing saturated aquifer sediment from near LB-EX-8 (fig. 1). Approximately 428,000 disintegrations per minute of ^{14}C-toluene (specific activity of 9.7 milliCuries per millimole) was added to triplicate 40-mL glass microcosms containing 5 mL of a sediment/ground-water slurry and 2.5 mL of ground water collected from a nearby contaminated well (LB-EX-RW, fig. 1). For aerobic and anaerobic treatments, dead controls (to account for abiotic evolution of $^{14}CO_2$) were made by sterilizing the prepared microcosm in an autoclave (121 °C for 1 hour) and adding 8 mM (millimolar) $HgCl_2$. Aerobic treatments for determining degradation rates of toluene were made without further modification.

Anaerobic degradation rates were estimated using vials prepared as above, but made anaerobic by purging the vials with helium for 3 minutes upon capping. At specified times during the experiment, vials were sacrificed by acidification with 45% H_3PO_4, the evolved $^{14}CO_2$ captured in a 3 M (molar) KOH solution suspended in the microcosm in a plastic bucket assembly, and the ^{14}C activity measured through liquid scintillation counting after addition to scintillation cocktail using a 1600TR liquid scintillation counter. The ^{14}C activities were corrected with dead controls, background radiation, activity at time point t=0, and counting efficiency. Activities are reported as a percentage recovered of the added label.

The microbial degradation rate of benzene was not measured in the laboratory using the radiolabel approach described above. Rather, the digital solute-transport model SUTRA (Saturated and Unsaturated TRAnsport) (Voss, 1984) was used to estimate an anaerobic benzene biodegradation rate by performing iterative calibration simulations to reproduce benzene concentrations observed in 1993 and 1994.

QUANTIFICATION OF HYDROLOGIC, GEOCHEMICAL, AND MICROBIAL PARAMETERS

The results of the hydrologic, geochemical, and microbial investigations are presented in this section. The hydrology and hydrogeologic framework and ground-water chemistry data are presented, as well as the adsorption and microbial degradation rates as determined in field and laboratory studies.

Hydrologic and Hydrogeologic Framework

The position of the water table in the shallow aquifer system was previously documented during contaminant assessment activities conducted in March and April 1993 (U.S. Navy Department, 1993) (fig. 3). In addition, the elevation of the top of each well casing was determined by survey. Water levels were measured using a steel tape on March 10, 1994 (fig. 4). In general, the water table is between 10 and 13 ft below land surface, and in a few places, as much as 17 ft below land surface. The generalized direction of ground-water flow in the shallow aquifer system is toward the south and west, away from the study site. The area of potential ground-water discharge from the shallow aquifer system is the Broad River (fig. 1), located approximately 3,600 ft west of the site boundary.

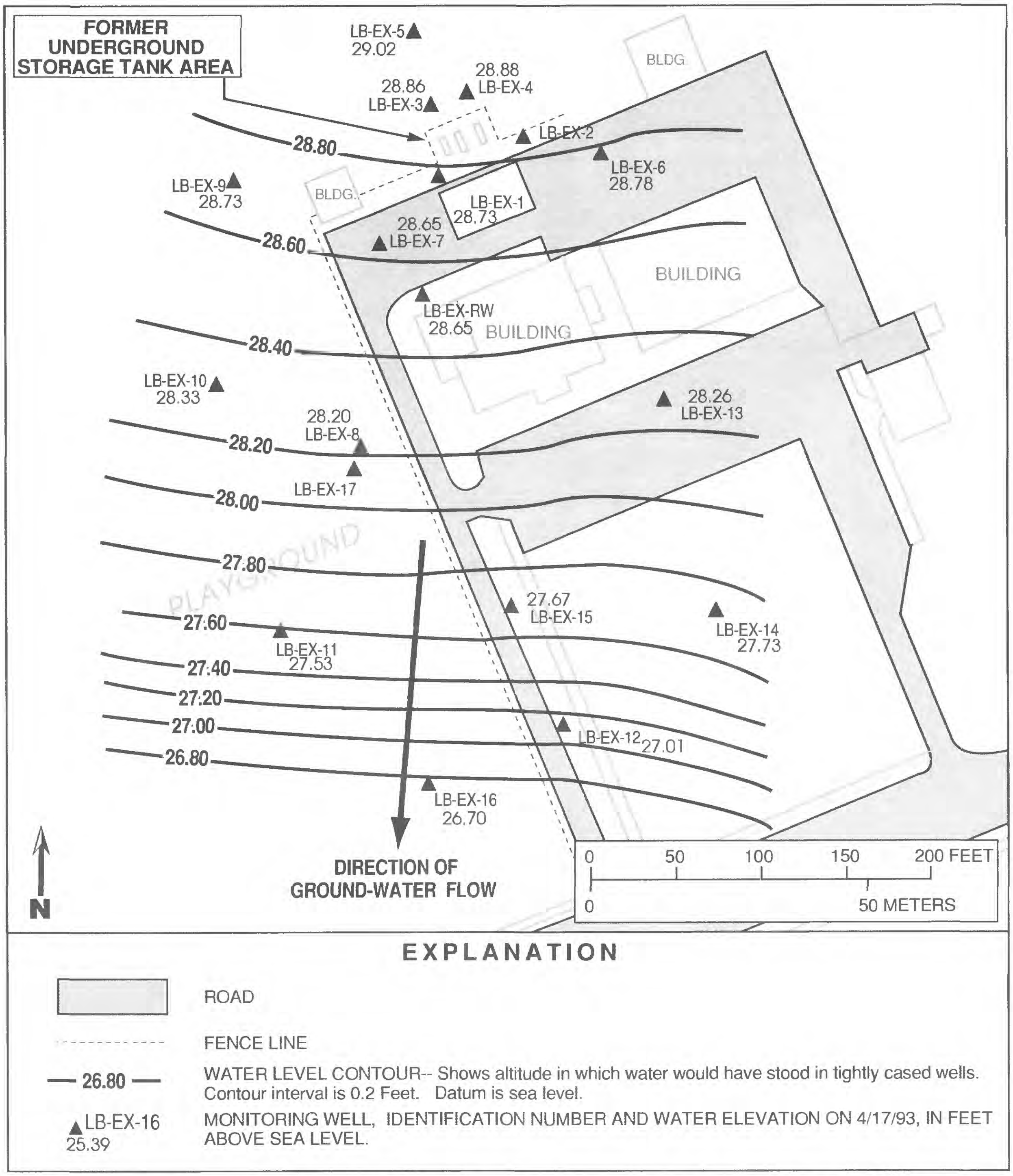

Figure 3. The water table in the shallow aquifer system, Laurel Bay Exchange, Marine Corps Air Station Beaufort, S.C., April 17, 1993 (from U.S. Navy Department,1993).

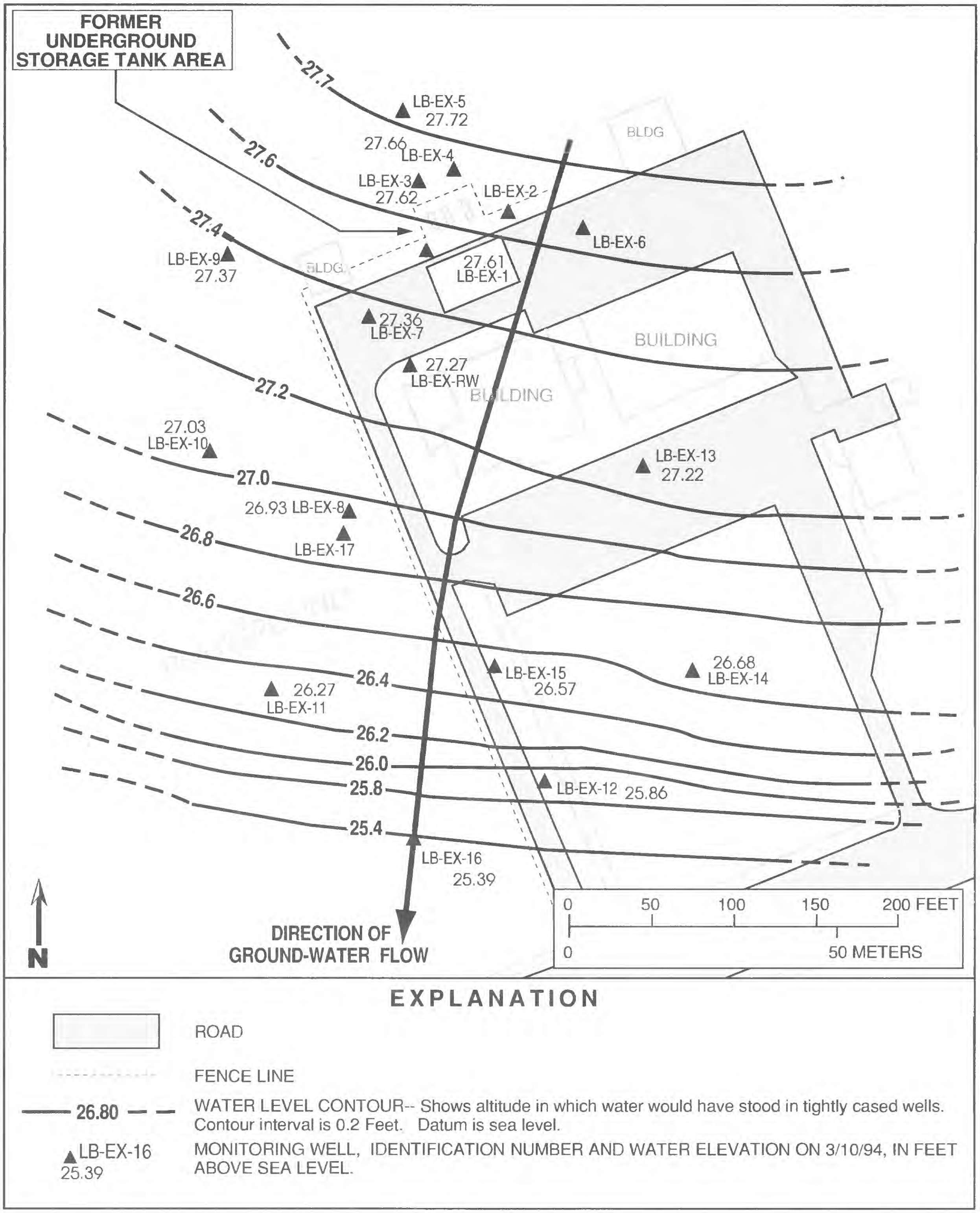

Figure 4. The water table in the shallow aquifer system, Laurel Bay Exchange, Marine Corps Air Station Beaufort, S.C., March 10, 1994.

The surficial aquifer system beneath the study site is comprised of fine-to-coarse grained sands with very few clay lenses, and is characterized by relatively high hydraulic conductivities. Rising-head aquifer tests conducted on four individual monitoring wells during the contamination assessment indicated an average hydraulic conductivity of 11.1 ft/d (U.S. Navy Department, 1993).

The rate of ground-water movement can be determined using Darcy's equation:

$$v = K\,(dh/dx)/n, \tag{1}$$

where

v is the average velocity of ground-water flow, in feet per day;

K is the average hydraulic conductivity, in feet per day;

dh/dx is the hydraulic gradient determined between two wells, dimensionless; and,

n is the aquifer sediment porosity, dimensionless.

A conservative estimate of the rate of ground-water flow can be determined by comparing the flow at the steepest hydraulic gradient with the flow at the shallowest hydraulic gradient. At the site, however, hydraulic gradients are uniform over the study area. The water level north of the site at LB-EX-4 (fig. 4) was 27.66 ft above sea level on March 10, 1994, and the water level south of the site at LB-EX-11 (about 300 ft from LB-EX-4) was 26.27 ft above sea level. A representative hydraulic gradient of 0.0046 ft/ft was determined between these two wells. Assuming a porosity of 30 percent for fine-grained sand, and using the average hydraulic conductivity of 11.1 ft/d, an estimate of the average ground-water flow of 0.170 ft/d, or about 62 ft/yr was calculated.

Ground-Water Chemistry

Concentrations of BTEX and MTBE were measured in ground-water monitoring wells at Laurel Bay (table 1). Concentrations of benzene in ground water ranged from below detection limits (BD) to 9,450 µg/L. Concentrations of toluene ranged from BD to 22,500 µg/L. Concentrations of ethylbenzene and total xylenes ranged from BD to 3,100 µg/L and from BD to 19,350 µg/L, respectively. Concentrations of MTBE in ground water ranged from BD to 251,000 µg/L.

Table 1.--*Concentrations of benzene, toluene, ethylbenzene, total xylenes, and methyl-tert-butyl-ether in ground water from monitoring wells at the Laurel Bay Exchange, Marine Corps Air Station Beaufort, S.C., March 11, 1994*

[µg/L, micrograms per liter; BD, below detection limit; MTBE, methyl-tert-butyl-ether; <, less than]

Monitoring well number (fig. 4)	Benzene (µg/L)	Toluene (µg/L)	Ethylbenzene (µg/L)	Xylene (total) (µg/L)	MTBE (µg/L)
LB-EX-1	8,450	20,600	<5	13,850	15,400
LB-EX-3	6.1	22.2	<5	258	22.2
LB-EX-4	BD	BD	BD	BD	BD
LB-EX-5	BD	BD	BD	BD	BD
LB-EX-7	9,450	22,300	3,100	15,100	251,000
LB-EX-8	9,180	22,500	2,400	19,350	26,700
LB-EX-9	36.6	132	11.8	60.7	54.4
LB-EX-10	BD	BD	BD	BD	BD
LB-EX-11	BD	BD	BD	BD	BD
LB-EX-12	BD	BD	BD	BD	BD
LB-EX-13	BD	BD	BD	BD	BD
LB-EX-14	BD	BD	BD	BD	BD
LB-EX-15	6.7	6.1	5.9	11.4	BD
LB-EX-16	6.5	BD	BD	BD	800
LB-EX-RW	8,650	16,100	BD	7,900	70,000

Based on the solubility differences between BTEX compounds compared to MTBE (table 2), two overlapping, elliptically shaped plumes can be delineated (fig. 5). The plumes of BTEX and MTBE developed simultaneously from a common source but have moved differentially in ground water in response primarily to differences in characteristic adsorption, solubility, and degradation properties. The BTEX plume is delineated by concentrations exceeding detection in monitoring wells LB-EX-1, 3, 7, 8, 9, 15, 16, and RW. By March 1994, this plume has advanced approximately 350 ft from the source area, and is about 180 ft wide. The plume of MTBE is delineated by concentrations exceeding detection in monitoring wells LB-EX-1, 3, 7, 8, 9, 16, and RW. The plume has advanced approximately 350 ft from the source area, and is about 180 ft wide. Wells upgradient from the source area (LB-EX-4 and 5) had no detectable BTEX or MTBE. Wells adjacent to the plume boundaries (LB-EX-10, 11, 12, 13, and 14) had no detectable BTEX or MTBE concentrations.

Table 2.--*Solubilities of benzene, toluene, ethylbenzene, o-xylene, and methyl-tert-butyl-ether in ground water at 25 degrees Celsius*

[mg/L, milligram per liter]

Compound	Solubility in ground water (mg/L)
Benzene	1,800
Toluene	535
Ethylbenzene	152
o-Xylene	170
Methyl-tert-butyl-ether	20,000

The 1994 BTEX plume has migrated about 350 ft from the source area since detection in September 1991. Given that the ground-water flow rate is roughly 70 ft/yr, and if no adsorption or microbial degradation were retarding the movement of BTEX from the source area, then the plume should have moved about 210 ft if the plume was released at the time of detection. Therefore, the plume may have been released 1 to 2 years before September 1991.

Evidence of the plume moving away from the source area is apparent when comparing the 1994 water-chemistry sampling results with those from March and April 1993 (U.S. Navy Department, 1993). In the most contaminated well, LB-EX-1, benzene and toluene concentrations were 16,000 and 43,000 μg/L, respectively, in 1993. One year later, they were 8,450 and 20,600 μg/L, respectively. This reduction does not represent depletion by degradation only; rather, it also represents ground-water transport as observed by increases in benzene and toluene concentrations in wells downgradient of LB-EX-1. For example, in LB-EX-8, benzene, toluene, and MTBE increased in one year from 1,700 to 9,180 μg/L, 4,000 to 22,500 μg/L, and 18,000 to 26,700 μg/L, respectively. This apparent movement from the source area is exhibited by increasing toluene concentrations away from the underground storage tanks to about 150 ft, beyond which no toluene is observed in monitoring wells farther downgradient (fig. 6).

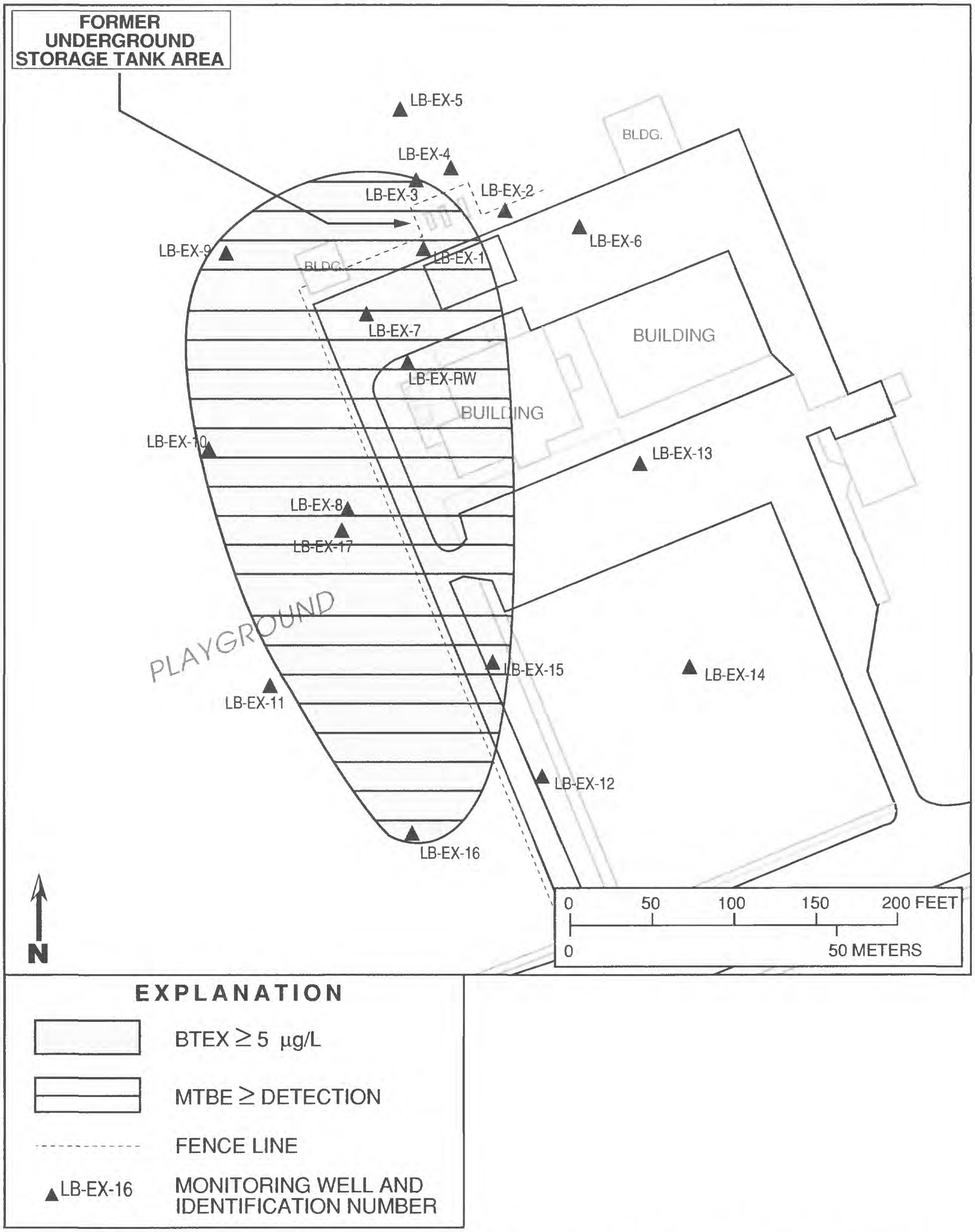

Figure 5. The location and geometry of the benzene, toluene, ethylbenzene, total xylene (BTEX), and methyl-tert-butyl ether (MTBE) plumes, Laurel Bay Exchange, Marine Corps Air Station Beaufort, S.C., March 11, 1994.

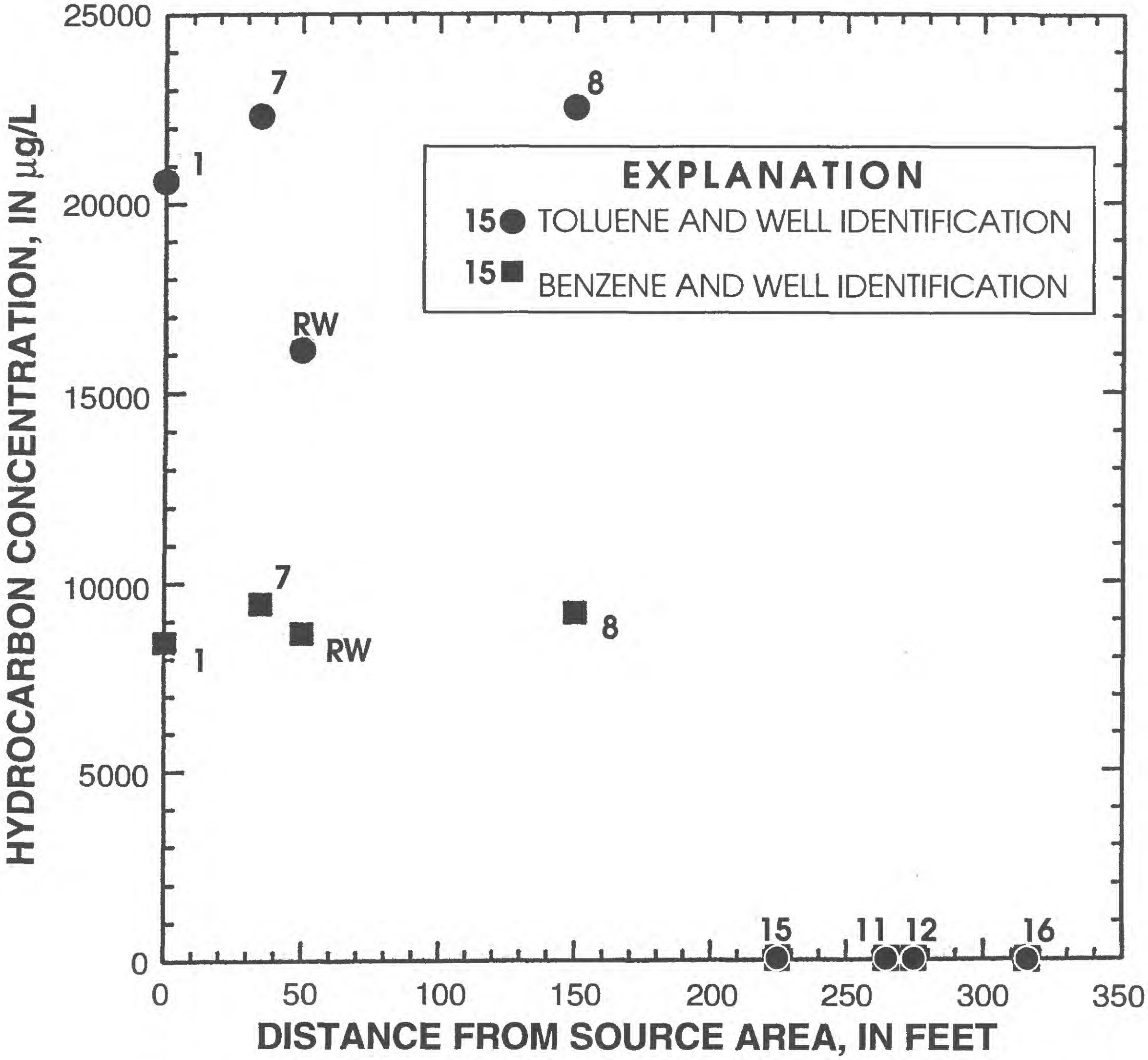

Figure 6. Relation between hydrocarbon concentrations and distance from the source area, March 11, 1994.

Detectable concentrations of MTBE, an anti-knock compound added to gasoline after 1979, have spread a considerable distance since leak detection in September 1991. Compared to BTEX compounds, MTBE is extremely soluble (table 2), is not adsorbed by aquifer material, and is believed to remain undegraded by microorganisms (Mormile and others, 1994). As such, it is often detected beyond BTEX plumes or at higher concentrations at contaminated sites. At Laurel Bay, a higher concentration (800 µg/L) than benzene (6.5 µg/L) is detected in the well farthest from the plume source. Because MTBE is currently an unregulated compound, no degradation studies using MTBE were performed.

Concentrations of dissolved oxygen (DO), Fe(II), and sulfide were determined in ground water, as well as pH and temperature (table 3). The ground water sampled in the shallow subsurface beneath the site was generally aerobic in wells not affected by petroleum hydrocarbons (average dissolved-oxygen concentration of 4.16 mg/L), and contained very little sulfide. In wells contaminated with petroleum hydrocarbons, however, dissolved oxygen was low, and dissolved Fe(II) concentrations were relatively high. These high concentrations of dissolved Fe(II) associated with the presence of organic contaminants result from the anaerobic microbial Fe(III) reduction of petroleum hydrocarbons in anoxic ground water (Lovley and others, 1989).

The concentrations for all cations analyzed in ground water beneath the study site are generally low and were not diagnostic of significant geochemical reactions (table 4). These concentrations primarily reflect the composition of rainwater at the site that has not had sufficient time following infiltration to the water table to react with the aquifer material, which itself has been highly leached with time.

Concentrations of anions in ground water were also determined (table 5). Concentrations of chloride do not seem to have any correlation with the presence of hydrocarbon contamination. Concentrations of bromide, although low, are higher at the contaminated wells than in uncontaminated wells. A possible source of this bromide could be the bromine used as a catalyst during the manufacture of gasoline. Concentrations of nitrate are low at the site, and would generally tend to limit the use of nitrate reduction for microbial degradation of hydrocarbons in the anaerobic part of the aquifer. The highest concentrations of nitrate are in water from two wells drilled in a grassy area of the site, and could be explained by the use of fertilizers during sod emplacement. Comparison of the low concentrations of nitrate (table 5) with the relatively higher concentrations of ammonium (table 4) reveals that most of the dissolved organic nitrogen in this shallow aquifer system is present as reduced ammonium. There is a correlation between increasing hydrocarbon contamination and lower sulfate values, but it is not uniform across all wells. The lowest concentrations of sulfate (0.82 and 0.99 mg/L for LB-EX-RW and LB-EX-7, respectively), in water from these contaminated wells may reflect sulfate reduction of petroleum hydrocarbons by the microbial community. However, sulfate-reduction by-products such as sulfide were below detection at these wells (table 3). Concentrations of phosphate were below detection in ground water from the monitoring wells. This lack of an essential nutrient for microbial protein synthesis may limit microbial metabolism.

Concentrations of dissolved inorganic carbon (DIC) and methane (CH_4) in ground water were determined at the site (table 6). DIC concentrations in ground water tended to increase as petroleum hydrocarbon contamination increased and dissolved-oxygen concentration decreased (fig. 7). Because DIC is comprised of inorganic forms of carbon, such as CO_2, the high level of DIC in contaminated areas reflects the microbial mineralization of organic compounds to CO_2. Concentrations of DIC also show a direct relation to an increase in dissolved Fe(II) in ground water (fig. 8). This provides an additional line of evidence that microbial Fe(III) reduction is a predominant terminal electron-accepting process (TEAP) in the shallow, anaerobic part of the contaminated aquifer. No methane was detected in any of the samples analyzed. The lack of methane suggests that although anaerobic conditions prevail in the contaminated part of theaquifer, methanogenic pathways of degradation are not being utilized by the microbial community.

Table 3.--*Concentrations of dissolved oxygen, ferrous iron, and sulfide in ground water, and field values of pH and temperature of ground water from monitoring wells at the Laurel Bay Exchange, Marine Corps Air Station Beaufort, S.C., March 11, 1994*

[mg/L, milligrams per liter; °C, degrees Celsius; BD, below detection limit; ND, no data collected; <, less than]

Monitoring well number (fig. 4)	Dissolved oxygen[a] (mg/L)	Ferrous iron[b] (mg/L)	Sulfide[c] (mg/L)	pH[d]	Temperature[d] (°C)
LB-EX-1	0	19.8	ND	6.12	19.7
LB-EX-3	2.18	.7	ND	4.90	18.6
LB-EX-4	5.34	.6	ND	6.97	16.1
LB-EX-5	5.07	BD	ND	4.63	17.9
LB-EX-7	0	20.0	ND	5.98	20.2
LB-EX-8	0	6.8	ND	5.78	17.7
LB-EX-9	4.11	BD	ND	4.76	17.2
LB-EX-10	2.93	BD	ND	5.75	17.8
LB-EX-11	4.66	BD	ND	4.77	17.2
LB-EX-12	4.43	BD	ND	5.30	16.3
LB-EX-13	5.91	ND	ND	7.56	17.0
LB-EX-14	5.30	ND	ND	7.30	17.1
LB-EX-15	.90	2.8	ND	5.53	16.3
LB-EX-16	4.92	BD	ND	4.50	16.8
LB-EX-RW	0	9.8	<.02	5.97	20.8

a. Dissolved oxygen was measured using the Winkler titration method (Hach Company, 1989).
b. Ferrous iron was measured using a Hach colormetric kit (Stookey, 1970).
c. Sulfide was measured using a Hach colormetric kit (Hach Company, 1989).
d. pH and temperature were measured using a Beckmann pH/temperature probe.

Table 4.--*Concentrations of cations in ground water from monitoring wells at the Laurel Bay Exchange, Marine Corps Air Station Beaufort, S.C., March 11, 1994*

[mg/L, milligrams per liter; R, replicate sample; BD, below detection limit]

Monitoring well number (fig. 4)	Magnesium (Mg^{2+}) (mg/L)	Calcium (Ca^{2+}) (mg/L)	Sodium (Na^{+}) (mg/L)	Potassium (K^{+}) (mg/L)	Ammonium (NH^{+}) (mg/L)
LB-EX-1	0.67	35.14	7.05	4.54	9.25
LB-EX-3	1.27	3.77	3.72	.50	BD
LB-EX-4	.96	1.88	3.37	.27	BD
LB-EX-5	1.66	1.16	5.82	.16	BD
LB-EX-7	.69	7.49	3.51	1.48	5.18
LB-EX-7R	.72	7.22	3.54	1.37	4.79
LB-EX-8	1.85	10.56	5.69	.83	1.35
LB-EX-9	1.36	4.17	3.79	.25	BD
LB-EX-10	1.86	6.31	5.63	.29	BD
LB-EX-11	1.78	4.57	10.57	.61	Bd
LB-EX-12	1.06	4.81	3.88	.54	BD
LB-EX-13	2.07	3.57	23.02	.50	BD
LB-EX-14	1.83	1.91	4.09	.38	BD
LB-EX-15	1.71	12.34	18.18	1.74	BD
LB-EX-16	1.19	1.36	8.14	1.44	BD
LB-EX-RW	.99	14.46	4.00	1.86	2.64

Table 5.--*Concentrations of anions in ground water from monitoring wells at the Laurel Bay Exchange, Marine Corps Air Station Beaufort, S.C., March 11, 1994*

[mg/L, milligrams per liter; R, replicate sample; BD, below detection limit]

Monitoring well number (fig. 4)	Chloride (Cl^-) (mg/L)	Bromide (Br^-) (mg/L)	Nitrate (NO_3^-) (mg/L)	Phosphate (PO_4^{3-}) (mg/L)	Sulfate (SO_4^{2-}) (mg/L)
LB-EX-1	4.47	0.12	0.19	BD	8.14
LB-EX-3	8.19	BD	.39	BD	6.75
LB-EX-4	5.53	BD	.15	BD	5.60
LB-EX-5	9.26	BD	.05	BD	7.45
LB-EX-7	5.55	.27	BD	BD	.99
LB-EX-7R	5.44	.17	.04	BD	.95
LB-EX-8	9.04	.23	BD	BD	9.82
LB-EX-9	7.01	BD	.08	BD	12.12
LB-EX-10	11.11	BD	.07	BD	14.75
LB-EX-11	16.14	.15	.04	BD	14.84
LB-EX-12	6.87	.08	.07	BD	12.13
LB-EX-13	24.45	.15	6.36	BD	24.43
LB-EX-14	7.06	BD	2.66	BD	9.93
LB-EX-15	22.26	BD	.67	BD	27.88
LB-EX-16	12.02	.11	BD	BD	15.50
LB-EX-RW	2.89	.08	BD	BD	.82

Table 6.--*Concentrations of dissolved inorganic carbon and methane in ground water from monitoring wells at the Laurel Bay Enchange, Marine Corps Air Station Beaufort, S.C., March 11, 1994*

[mg/L, milligrams per liter; R, replicate sample; BD, below detection limit]

Monitoring well number (fig. 4)	Dissolved inorganic carbon (mg/L)	Methane (mg/L)
LB-EX-1	208.1	BD
LB-EX-3	113.7	BD
LB-EX-4	52.9	BD
LB-EX-5	18.7	BD
LB-EX-7	158.0	BD
LB-EX-7R	220.2	BD
LB-EX-8	132.6	BD
LB-EX-9	31.0	BD
LB-EX-10	34.4	BD
LB-EX-11	1.9	BD
LB-EX-12	44.2	BD
LB-EX-13	46.7	BD
LB-EX-14	33.3	BD
LB-EX-15	67.3	BD
LB-EX-16	28.8	BD
LB-EX-RW	251.1	BD

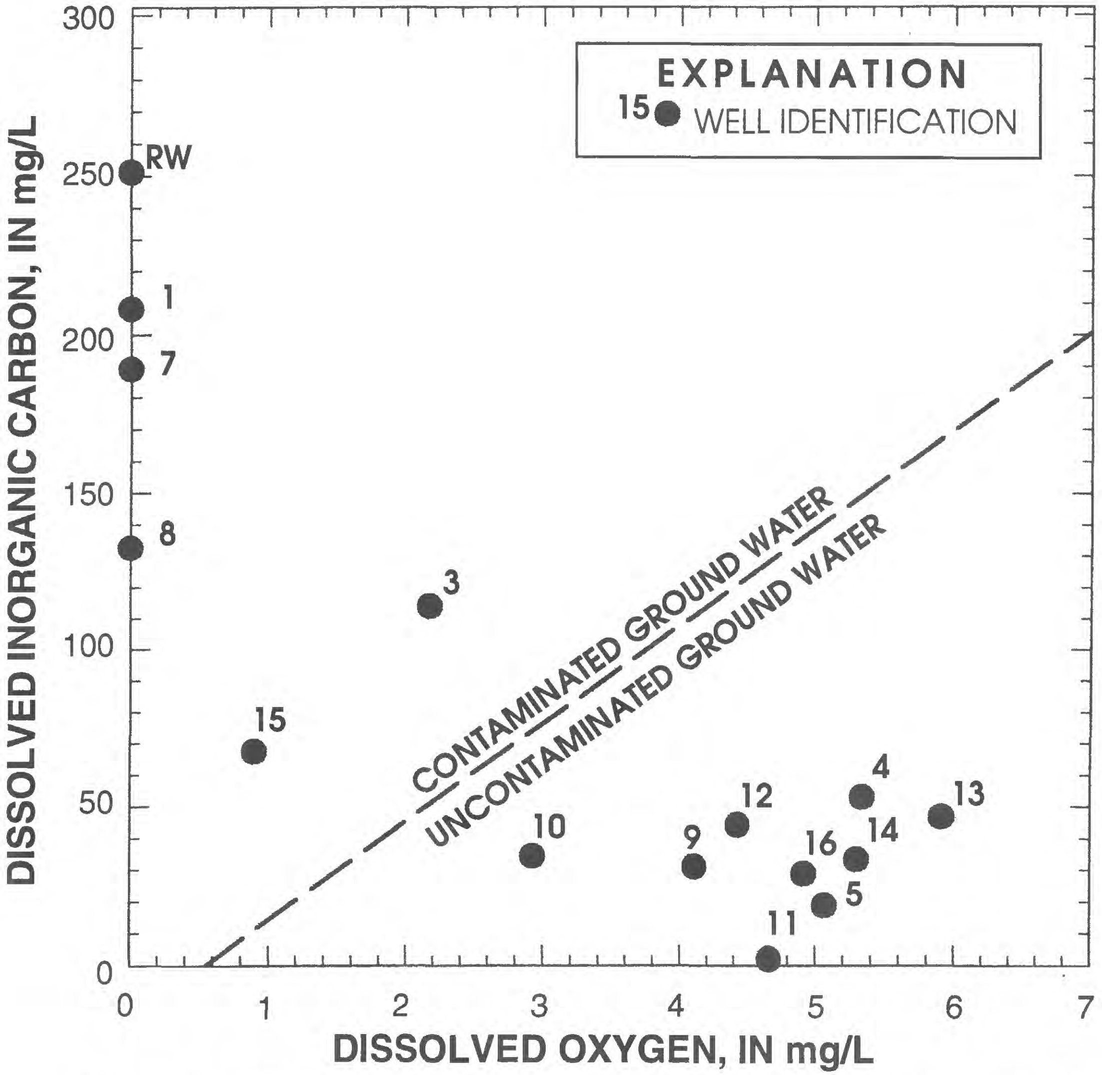

Figure 7. Relation between dissolved inorganic carbon and dissolved oxygen in contaminated and uncontaminated ground water, Laurel Bay Exchange, Marine Corps Air Station Beaufort, S.C., March 11, 1994.

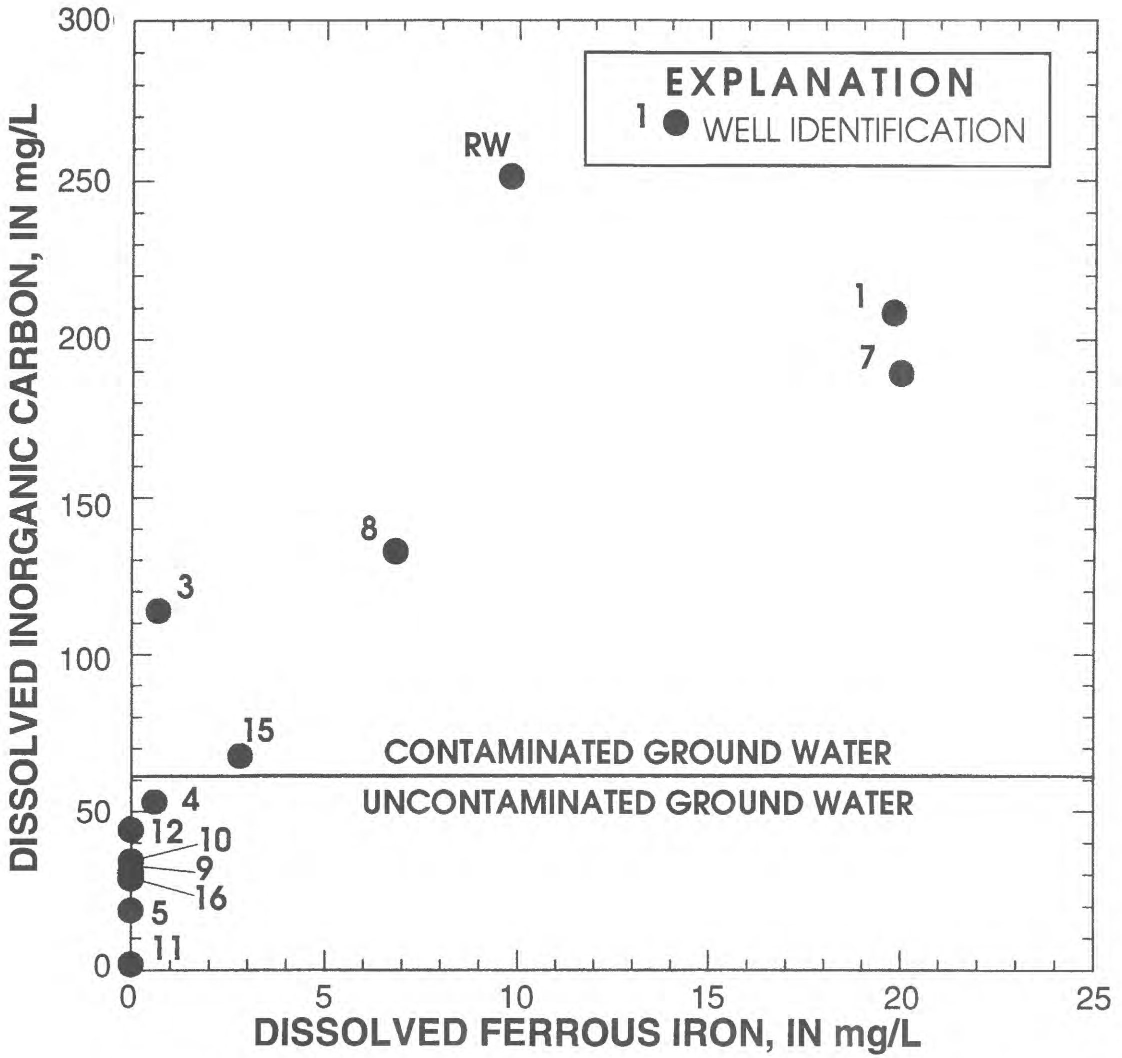

Figure 8. Relation between dissolved inorganic carbon and dissolved ferrous iron in contaminated and uncontaminated ground water, Laurel Bay Exchange, Marine Corps Air Station Beaufort, S.C., March 11, 1994.

The ground-water concentrations of particular anions and cations provide several lines of evidence that the petroleum hydrocarbons are undergoing intrinsic bioremediation in the shallow aquifer at Laurel Bay. The initial line of evidence is the lack of DO in the most contaminated monitoring wells (fig. 9). Oxidation of hydrocarbons through the microbial reduction of oxygen is the most efficiently used TEAP in the subsurface, and as such, rapidly decreases the DO concentration when petroleum hydrocarbons are released. There is an inverse relation between concentrations of toluene and benzene dissolved in ground water and DO (fig. 9); namely, high toluene and benzene concentrations result in low concentrations of DO and the same is true for the reverse. This relation has been observed at many sites involving the release of BTEX compounds (Chiang and others, 1989; McAllister and Chiang, 1994; and Chapelle and others, 1995).

Low concentrations of DO allow further oxidation of hydrocarbons to occur through the reduction of ferric iron as Fe(III). Ferric iron (and its hydroxides) forms a ubiquitous reddish coating on sand grains in shallow aerobic aquifers similar to the aquifer at Laurel Bay. The microbial reduction of the Fe(III) on sand grains accompanying the oxidation of petroleum hydrocarbons results in the release of dissolved Fe(II) into the ground water. Therefore, the relatively high concentrations of Fe(II) measured in wells lacking DO is an indication of microbial iron reduction (table 3).

The presence of DO and Fe(II) at the site indicate that at least two processes of aerobic and anaerobic microbial degradation are proceeding at the site. If DO is present, aerobic degradation will proceed until the DO is consumed. When DO levels are depressed, the Fe(III) present on the sand grains that comprise the shallow aquifer is reduced anaerobically. The fact that there is little geochemical evidence that the less efficient TEAPs of sulfate-reduction or methanogenesis are being utilized indicates the relatively young age of the plume (about 3 years). Additionally, iron reduction probably reverts to aerobic degradation after low concentrations of DO are replenished following infiltration of DO-charged rainwater.

Concentrations of DIC can also provide a geochemical line of evidence that microbial degradation of petroleum hydrocarbons is occurring at the study site for several reasons. First, DIC concentrations are higher in monitoring wells contaminated with petroleum hydrocarbons and lower in wells without contamination (fig. 7). This suggests that (1) the uncontaminated aquifer has very little sedimentary organic matter, and probably results in a carbon-limited microbial community; and (2) once an abundant supply of organic matter (petroleum hydrocarbons) is supplied, contaminants are mineralized to CO_2. Further examination of DIC concentrations implies that the major anaerobic process is iron reduction; concentration increases in DIC reflect a concomitant increase in Fe(II) concentrations (fig. 8). This is important from the standpoint that as BTEX compounds migrate with ground water, sufficient Fe(III) on the aquifer material will not be a limiting factor in the degradation of the contaminants.

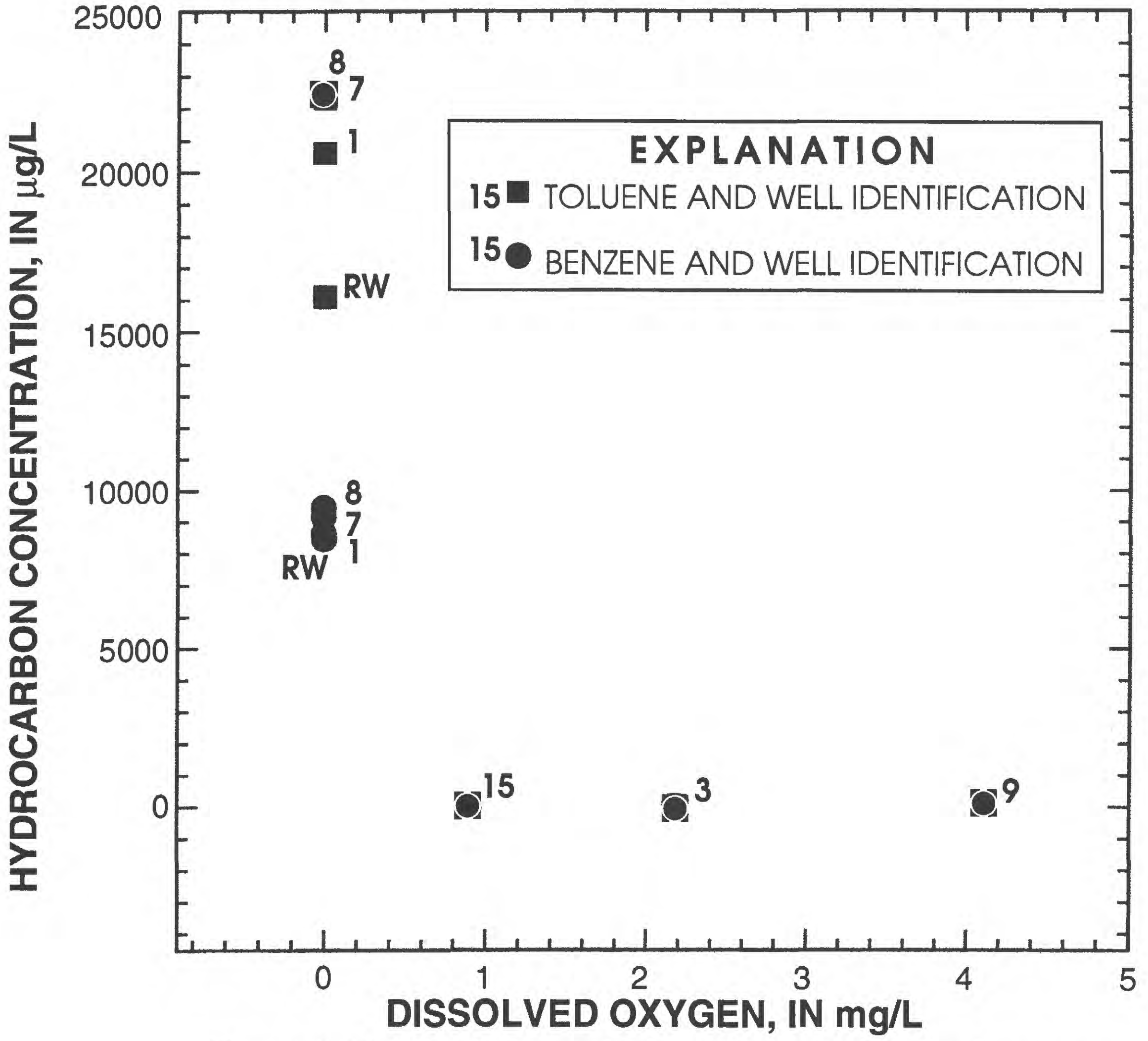

Figure 9. Relation between hydrocarbon and dissolved oxygen concentrations for benzene and toluene, March 11, 1994.

Adsorption Coefficient

Adsorption coefficients (K_{ad}) describe the potential for an organic hydrocarbon to be partitioned between an aqueous phase (ground water) and a solid phase (aquifer material). The higher the potential to be adsorbed onto aquifer material, the higher the K_{ad} value; the converse also holds. Such behavior can be expressed using a linear model of adsorption to predict adsorption capacity at a particular concentration. Values of K_{ad} determined for toluene in the fine-to-coarse grained, sedimentary organic-poor sand ranged from $K_{ad} = 2.0 \times 10^{-9}$ to 5.0×10^{-9} ft^3/mg, and were determined by regressing the adsorption data compared to concentration (fig. 10). Values of K_{ad} determined for benzene at the site ranged from $K_{ad} = 2.0 \times 10^{-9}$ to 1.0×10^{-8} ft^3/mg. These values are low and suggest that very little toluene or benzene will be adsorbed onto the aquifer material and that petroleum-hydrocarbon transport will not be retarded relative to ground-water flow. However, these low adsorption data also suggest that contaminated aquifer sediments will not be a significant source of contaminants to flowing ground water.

Microbial Degradation

A series of degradation experiments involving radiolabeled ^{14}C-toluene in laboratory microcosms were utilized to directly assess the microbial degradation of BTEX compounds in the shallow aquifer at the study site. Microcosm conditions were arranged to provide rates of toluene degradation under aerobic and anaerobic conditions. This approach allows meaningful interpretations to be made for the field conditions observed at the site.

The results of the radiolabeled experiments suggest an active microbial population at the site can degrade toluene. Toluene degradation rates under aerobic conditions were 200 times faster than rates measured under anaerobic conditions. For example, 14 percent of ^{14}C-toluene and 30 percent of ^{14}C-toluene was mineralized after 8 hours and 2 weeks upon starting the experiment, respectively (fig. 11A). Under anaerobic conditions, only 4 percent of the ^{14}C-toluene was mineralized after a period of 2 weeks (fig. 11B).

The microbial degradation of benzene was estimated using a digital solute-transport model. The benzene plume measured in April 1993 was simulated using the numerical model SUTRA (Voss, 1984). The distribution of benzene in ground water measured in 1994 could only be reproduced if an anaerobic microbial degradation rate of $K_{bio} = -0.00025\ d^{-1}$ was incorporated into the model. Although this indicates low rates of benzene biodegration, it is sufficient to measurably attenuate the benzene plume with time.

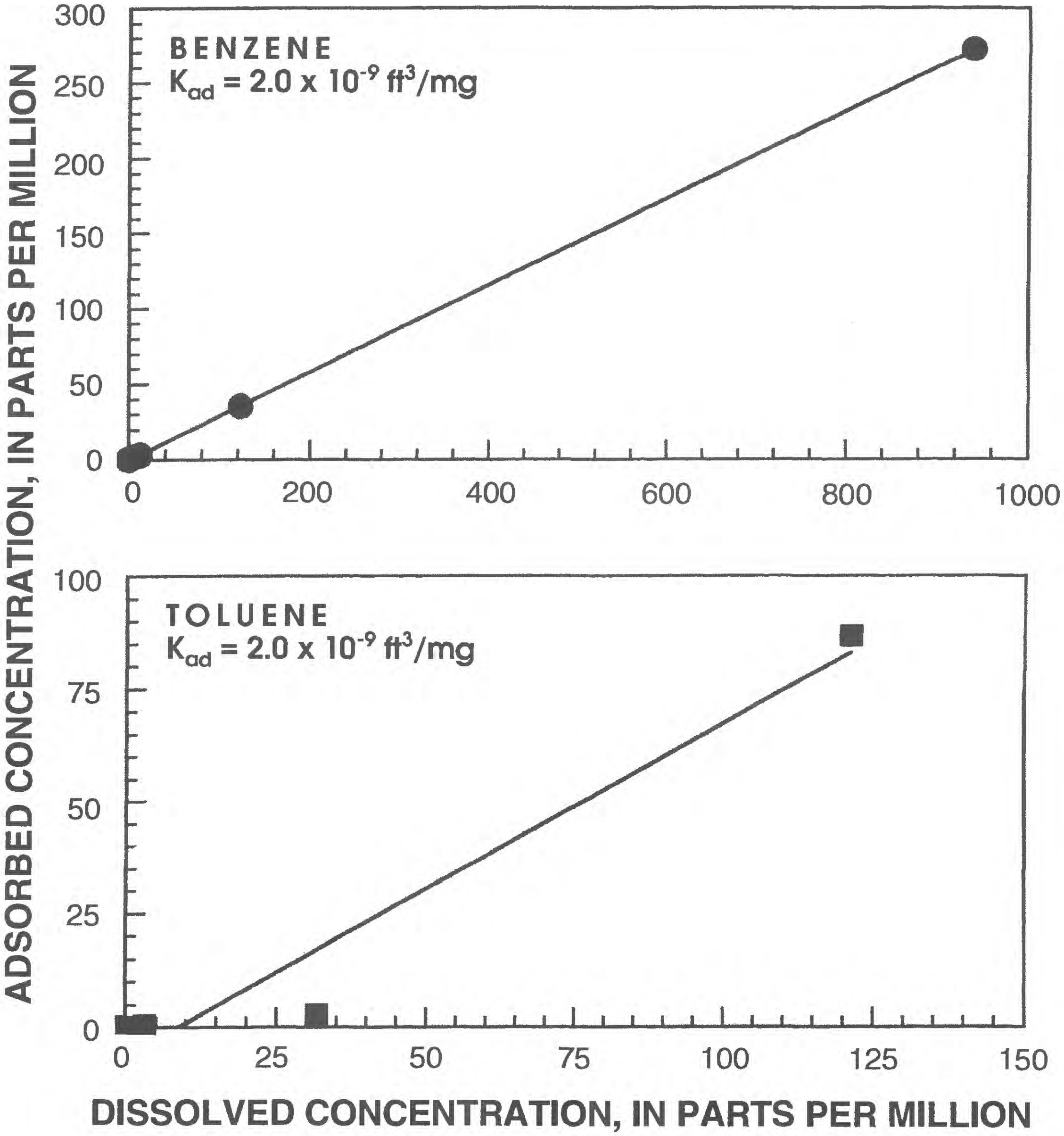

Figure 10. Relation between adsorbed and dissolved concentrations of benzene and toluene for aquifer sediments from Laurel Bay Exchange, Marine Corps Air Station Beaufort, S.C.

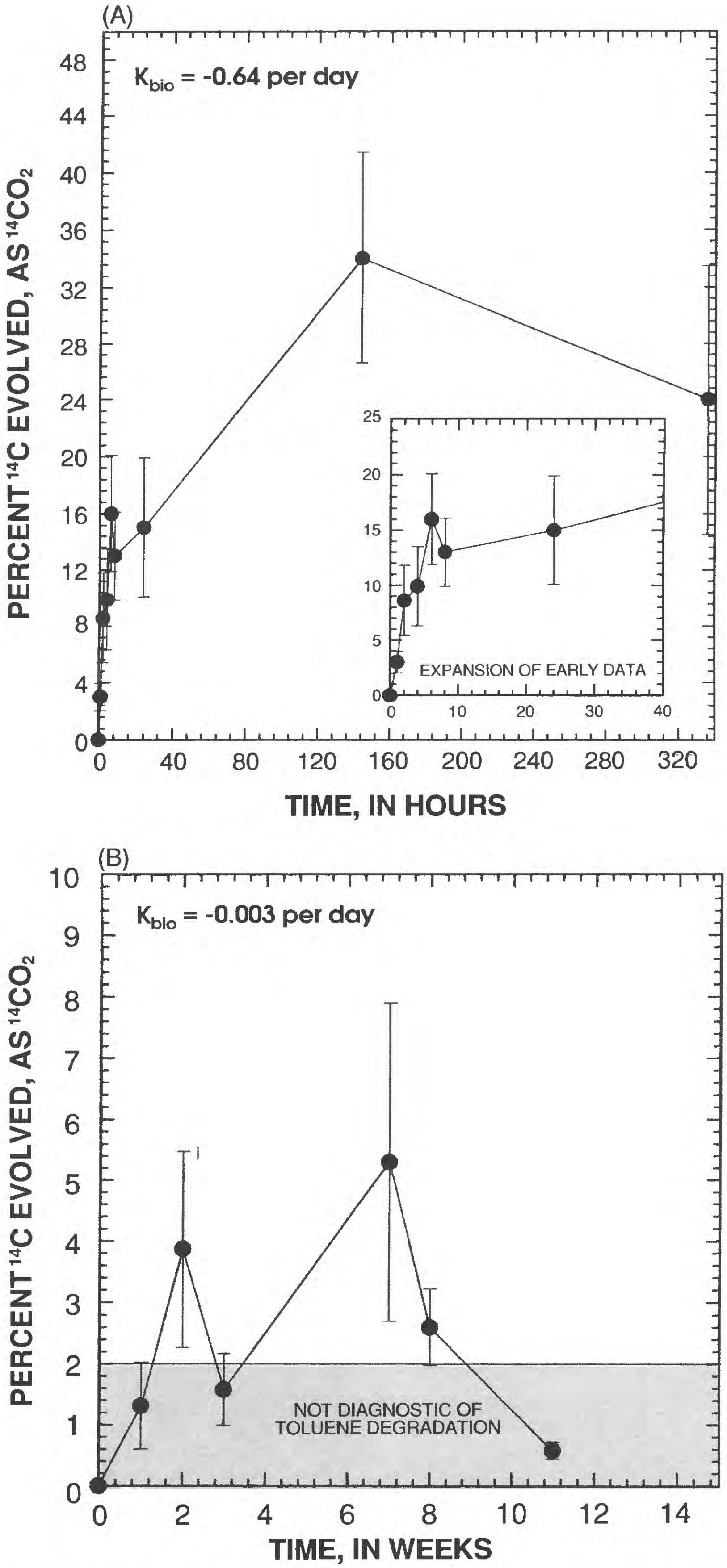

Figure 11. Mineralization rates of ^{14}C-toluene under (A) aerobic and (B) anaerobic aquifer conditions.

ASSESSMENT OF INTRINSIC BIOREMEDIATION

The migration of soluble contaminants in ground-water systems is affected by hydrologic, geochemical, and microbial processes. The principle hydrologic factors are the dispersion and advection of the contaminants in flowing ground water. There are a wide variety of geochemical processes that can affect the transport of contaminants including mineral precipitation/dissolution and adsorption/desorption reactions. Petroleum hydrocarbons in ground water are not, in general, subject to significant mineral precipitation reactions, so the most important geochemical process affecting concentrations of such compounds are sorption reactions. Finally, the microbial degradation of hydrocarbons can mineralize these toxic compounds into innocuous by-products.

Approach to Simulating Solute Transport

The effects of hydrologic, geochemical, and microbial processes on contaminant transport can be quantified using a mass balance equation that includes a component to describe each process. Where advection, sorption, and microbial degradation are the principal processes affecting transport, a one-dimensional equation may be written as:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} - SC^n - kC, \qquad (2)$$

where

C is concentration of the solute, in milligrams per liter;

t is time, in days;

D is the coefficient of hydrodynamic dispersion, in feet squared per day;

x is distance, in feet;

v is the velocity of ground-water flow, in feet per day;

S and n are adsorption isotherm parameters; and,

k is a first-order microbial degradation rate constant, in per day.

This equation is most readily solved by numerical methods. In this study, the two-dimensional solute-transport code SUTRA (Voss, 1984) was used to obtain solutions to equation (2) using the most realistic ranges of hydrologic, geochemical, and microbial conditions at Laurel Bay.

The hydrologic conditions at the site were simulated by assigning hydraulic conductivities measured using aquifer tests in single wells (U.S. Navy Department, 1993) and by using the water table observed on March 10, 1994. In comparing this water table with the one for April 1993 (U.S. Navy Department, 1993), the data indicate the older data showed water levels 2 ft higher than those measured in 1994. However, the two sets of data also show that the hydraulic gradients are quite similar (figs. 3 and 4). Therefore, no attempt was made to model a particular water table, and a constant hydraulic gradient was imposed on the modeled area, which significantly simplified the actual hydrologic system.

There are two distinct approaches to modeling complex hydrologic systems. The first, often called consolidative modeling, seeks to simulate every possible feature of a hydrologic system to obtain a unique solution. While conceptually appealing, consolidative modeling assumes that all relevant hydrologic parameters can be measured, and that spatial and temporal variabilities of these parameters can be defined. Such an approach comes into conflict with the uncertainties inherent to all hydrologic systems under observation. It is not possible, for example, to precisely measure the distribution of hydraulic conductivities at a site, so that uncertainties in model results are inevitable. When the uncertainties inherent in measuring all of the relevant hydrologic, geochemical, and microbial factors are taken into account, it is clear that to arrive at the single unique solution envisioned by consolidative modeling is not technically feasible.

The second approach to modeling hydrologic systems, called exploratory modeling, explicitly recognizes these inherent uncertainties. Rather than attempting to arrive at a single unique solution, exploratory modeling depicts the range of possible solutions based on the variability of the revelant parameters. For example, if the hydraulic conductivity (K_{aq}) is known to range two orders of magnitude, an exploratory model will evaluate solute transport for this range of K_{aq} so that the effects of this uncertainty can be described. The results of this approach, therefore, are useful for placing reasonable bounds on how a particular system can behave. Thus, it could be concluded that for a given range of possible K_{aq}, a particular solute could be transported distances dependent upon these ranges. Rather than attempting to define one solution, this approach attempts to define the reasonable range of solutions possible in a system.

For the purposes of assessing the efficiency of intrinsic bioremediation to contain contaminants, the exploratory modeling approach is most appropriate. In such an assessment, the most relevant question to be answered is whether contaminants will reach a point-of-contact under any possible conditions that might be feasible at the site. If it can be demonstrated that, given the range of parameters for a site, there is no combination that results in solute transport to a POC, then it can be concluded with a high degree of confidence that intrinsic bioremediation is a feasible remedial alternative. On the other hand, if the given range of parameters suggests that solute transport to a POC is possible, then intrinsic bioremediation is not a feasible alternative to contain contaminants. For this report, the exploratory modeling approach to solute transport is used.

Solute-Transport Simulations of Toluene Migration

The range of hydraulic gradients, hydraulic conductivities, adsorption isotherms, and microbial degradation rates were determined for the Laurel Bay site (table 7). The parameters of greatest uncertainty are K_{aq} and K_{bio}. The mean value of four K_{aq} measurements was 11.1 ft/d, but the standard deviation of 3.3 ft/d indicated significant variability resides in this measurement (U.S. Navy Department, 1993). Similarly, the measured microbial degradation rates of toluene varied between $K_{bio} = -0.003\ d^{-1}$ (anaerobic conditions) to $-0.640\ d^{-1}$ (aerobic conditions) and $K_{bio} = -0.00025\ d^{-1}$ for the anaerobic degradation of benzene. Given this variability, the modeling approach was to calculate the distribution of hydrocarbons for the possible extremes to evaluate the potential of solute transport to the nearest POC. To do this, a set of most probable values was selected, based on measurements made at the site (table 7), and used to construct a Standard Model. This model assumes that the water-table gradients remain constant (that is, the water-level distribution is the same as of March 10, 1994); that the aquifer remains anaerobic (that is, $K_{bio} = -0.003\ d^{-1}$ for toluene; $K_{bio} = -0.00025\ d^{-1}$ for benzene); and that the aquifer exhibits little adsorption capacity for toluene and benzene ($K_{ad} = 2.0 \times 10^{-9}\ ft^3/mg$). The modeled area is oriented so that the free-product source area is located on the upgradient side (fig. 12), and the nearest of the two POC (the property line to the south of the boundary of the site) is located on the downgradient side of the modeled area. The ultimate discharge area for ground water beneath the site (the Broad River) is not included in the model because of scale constraints. This model is not intended to represent actual values of parameters, but rather to provide a standard against which to compare the affects on solute transport from changing the parameters within the measured ranges.

The simulation of toluene transport and concentration distribution in 1994 based on the Standard Model (fig. 13) shows the development of a toluene plume from a constant source (free product leaching into ground water at a concentration of 50 mg/L) introduced at a known time (late 1991) in a sandy aquifer. The model is based on the best estimate for hydraulic conductivity ($K_{aq} = 11.1$ ft/d), predominantly anaerobic rates of toluene degradation ($K_{bio} = -0.003\ d^{-1}$), and toluene adsorption ($K_{ad} = 2.0 \times 10^{-9}\ ft^3/mg$). Ideally, the use of these parameters should closely approximate plume distribution similar to that observed during field sampling. The maximum extent of the simulated 1994 toluene plume (delineated by the 0.1 mg/L contour) reaches dimensions of 400 ft in length, which is 100 ft farther than the 300 ft that the toluene plume migrated in the field (fig. 5). The difference can be explained by the lack of wells in the downgradient area of the plume and absence of hydrocarbon concentration data in areas the simulation shows as being contaminated.

The Standard Model indicates that the toluene plume reaches steady-state conditions (no change in toluene concentrations over time) about 2001, when the rate of toluene migration is balanced by the rate of toluene degradation. As a result, the plume stops growing (figs. 14A-D). At steady state, toluene concentrations are contained to within 125 ft of the present plume boundary.

Table 7.--*Most probable values and best estimates for hydraulic gradient, hydraulic conductivity, microbial degradation, and adsorption for site conditions at the Laurel Bay Exchange, Marine Corps Air Station Beaufort, S.C.*

[ft/ft, foot per foot; ft/d, feet per day; ft^3/mg, cubic feet per milligram; --, no data]

Parameter	Most probable values		
	High estimate	Low estimate	Best estimate
Hydraulic gradient (ft/ft)	0.0046	0.0046	0.0046
Hydraulic conductivity (ft/d)[a]	17.3	8.9	11.1
Microbial degradation rate (toluene) (per day)[b]	-0.640 (aerobic)	-0.003 (anaerobic)	-0.003 (anaerobic)
Adsorption rate (toluene) (ft^3/ mg)[b]	5.0×10^{-9}	$2.0 \text{ X } 10^{-9}$	2.0×10^{-9}
Microbial degradation rate (benzene) (per day)[b]	-- (aerobic)	-0.00025 (anaerobic)	-0.00025 (anaerobic)
Adsorption rate (benzene) (ft^3/mg)[b]	1.0×10^{-8}	2.0×10^{-9}	2.0×10^{-9}

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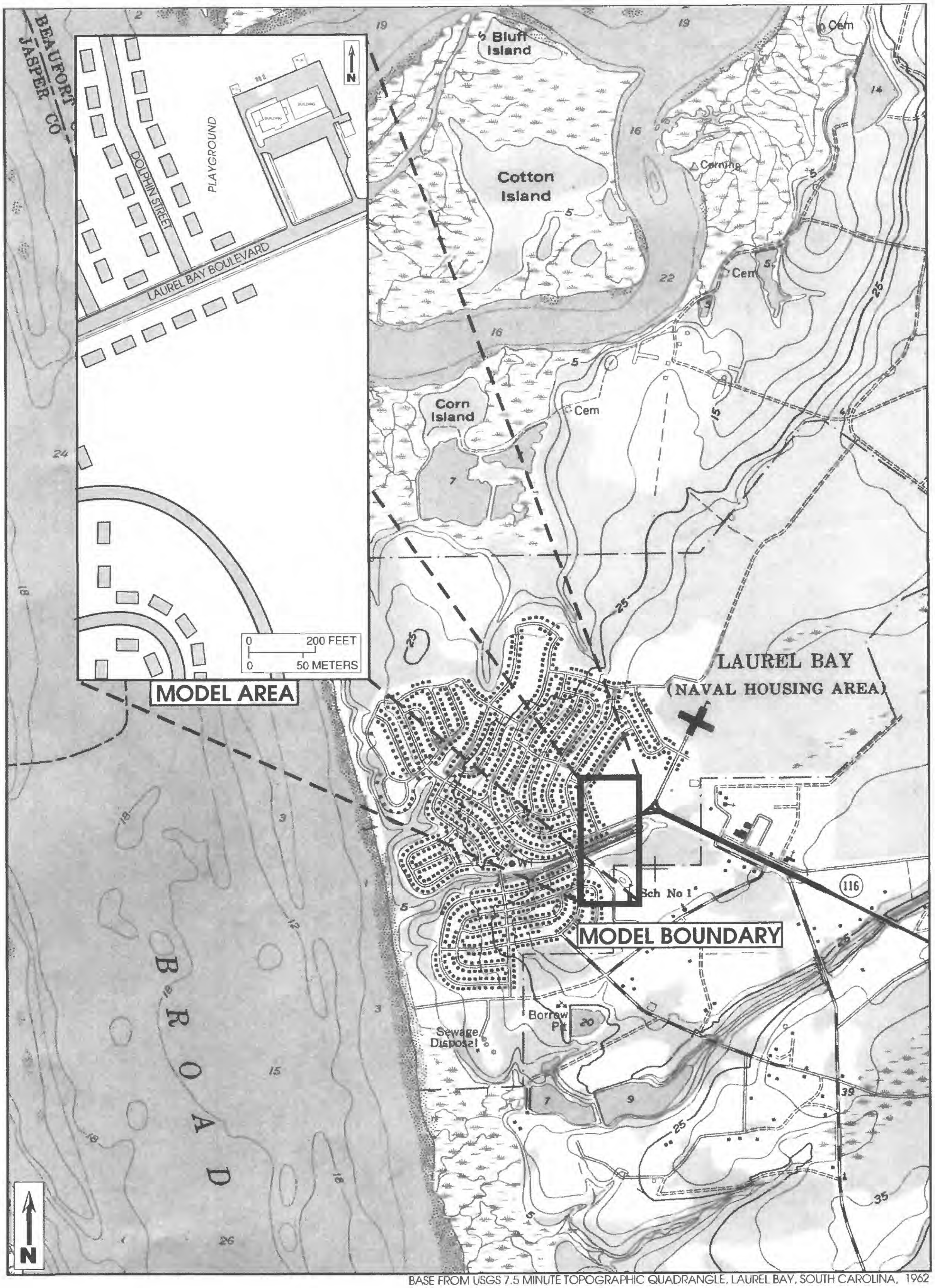
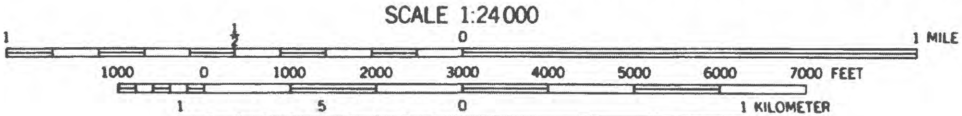
a. U.S. Navy Department, 1993.

b. U.S. Geological Survey Microbial Studies Group Laboratory, Columbia, S.C.



BASE FROM USGS 7.5 MINUTE TOPOGRAPHIC QUADRANGLE, LAUREL BAY, SOUTH CAROLINA, 1962



CONTOUR INTERVAL 10 FEET
NATIONAL GEODETIC VERTICAL DATUM OF 1929

Figure 12. Locations of the **S**aturated and **U**nsaturated **TRA**nsport (SUTRA) model area.

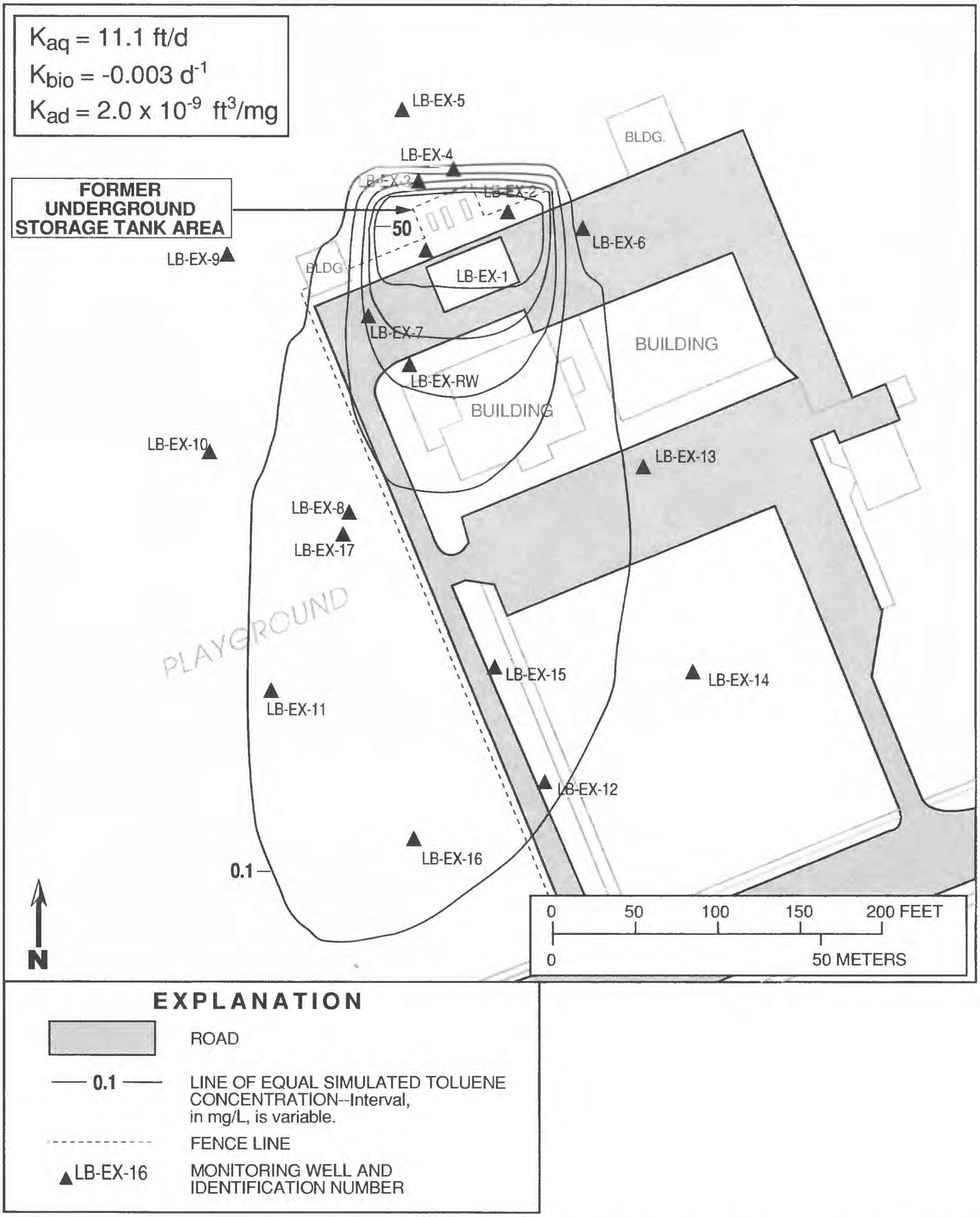
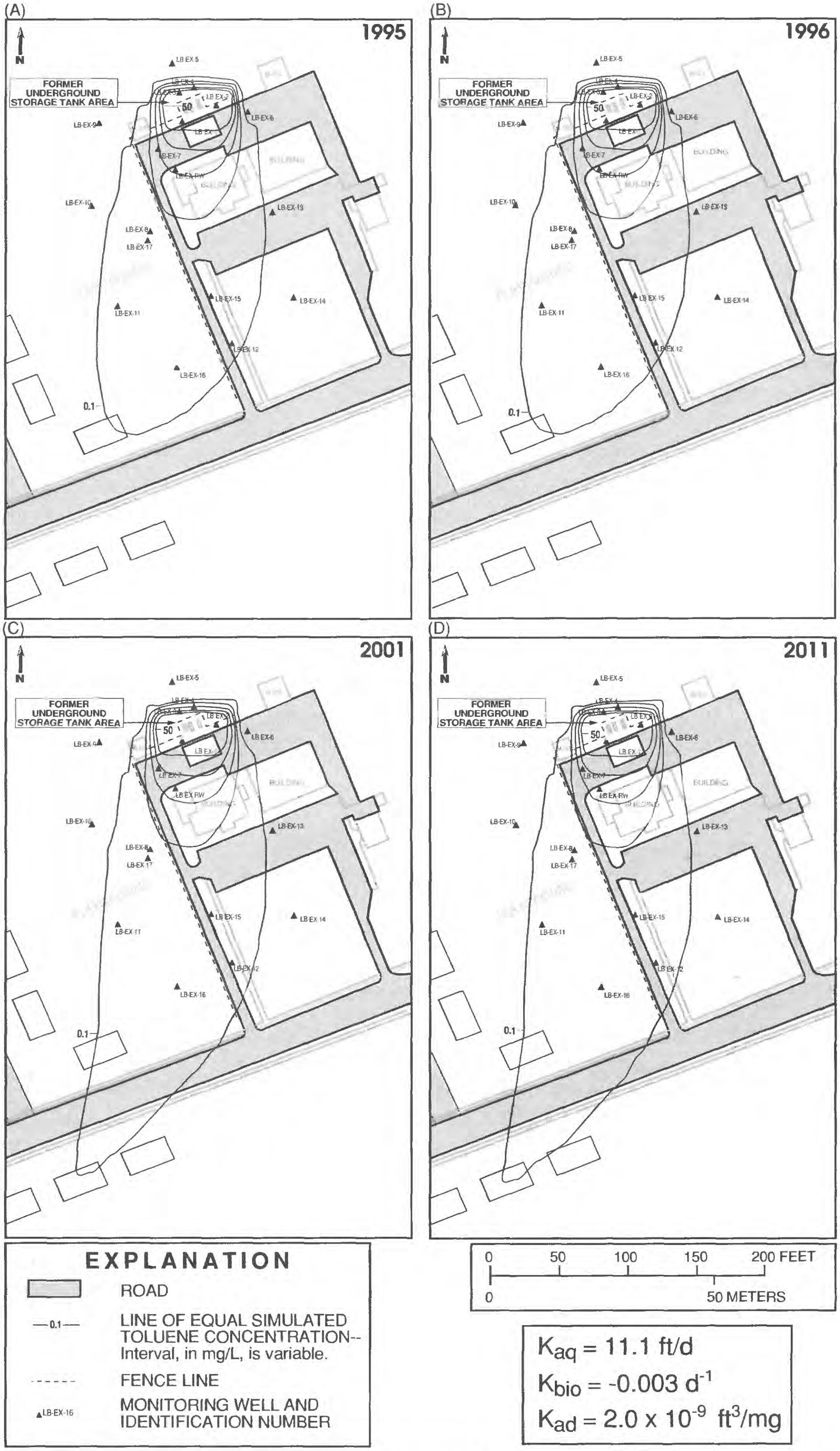


Figure 13. Simulated 1994 distribution of toluene for values of the Standard Model at Laurel Bay Exchange, Marine Corps Air Station Beaufort, S.C.



K_{aq} = 11.1 ft/d

K_{bio} = -0.003 d^{-1}

K_{ad} = 2.0 x 10^{-9} ft^3/mg

Figure 14. Simulated toluene plume in (A) 1995, (B) 1996, (C) 2001, and (D) 2011 at Laurel Bay Exchange, Marine Corps Air Station Beaufort, S.C., using the Standard Model.

A worst-case scenario of toluene transport from a constant source in 1991 to 1994 can be simulated using no biodegradation or adsorption, and is considered to be the Conservative Model. Because there is no retardation of the contaminant by either adsorption or biodegradation processes, the simulated plume migrates no slower than the rate of the ground-water velocity (fig. 15). Simulations show, however, that the toluene plume migrates farther than that predicted by simple advection, as a result of the dispersive effects of the silty sand grains in the aquifer, that cause some ground-water flowpaths to be longer than others. The maximum extent of the toluene plume, as delineated by the isoconcentration line of 0.1 mg/L, has migrated about 600 ft from the source area by 1994 (fig. 15). A transport rate of about 200 ft/yr can be calculated, which would suggest toluene transport to the Broad River in about 18 years. This Conservative Model also indicates that the toe of the toluene plume would enlarge continuously over time.

The affects of varying hydraulic conductivity (K_{aq}) in simulations using the Standard Model on the dimensions of the simulated toluene plume were determined. The simulated distribution of toluene assuming the aquifer system has uniformly low (K_{aq} = 8.9 ft/d) and high (K_{aq} = 17.3 ft/d) hydraulic conductivities are shown in figure 16A and B, respectively. The higher K_{aq} results in a larger (by about 150 ft) plume, because of a higher rate of ground-water flow.

Laboratory studies performed on sediments from the contaminated part of the shallow aquifer indicate that rates of toluene biodegradation could be as low as $K_{bio} = -0.003\ d^{-1}$ (anaerobic conditions) or as high as $K_{bio} = -0.640\ d^{-1}$ (aerobic conditions). The Standard Model describes the 1994 distribution observed with a low ($K_{bio} = -0.003\ d^{-1}$) rate of degradation (fig. 17A). Increasing the degradation rate to $K_{bio} = -0.64\ d^{-1}$ results in toluene containment in 1994 to within 50 ft of the source area (fig. 17B).

The similarity of the Standard Model results (with uniformly anaerobic rates of biodegradation) with geochemical conditions in the field indicates that there is significantly more anaerobic degradation in the plume body than aerobic degradation. There is probably some aerobic degradation following delivery of oxygen-charged rainwater to the plume, which would become temporarily aerobic until all the DO is consumed. This does indicate, however, that the anaerobic plume is encountering oxygenated ground water at its boundaries and in the direction of migration toward POC's.

Laboratory studies indicate that the adsorption capacity of the sandy aquifer material with respect to toluene is uniformly low ($K_{ad} = 2.0 \times 10^{-9}$ to $5.0 \times 10^{-9}\ ft^3/mg$). This small range of values was determined by varying the value and showing its affect on contaminant migration. Increasing the K_{ad} in the Standard Model to the higher value of $5.0 \times 10^{-9}\ ft^3/mg$ did not appreciably reduce the migration of contaminants (fig. 18A) when compared with results using $K_{ad} = 2.0 \times 10^{-9}\ ft^3/mg$ (fig. 18B). These results indicate that adsorption does not play a major role in the retardation of toluene at the site.

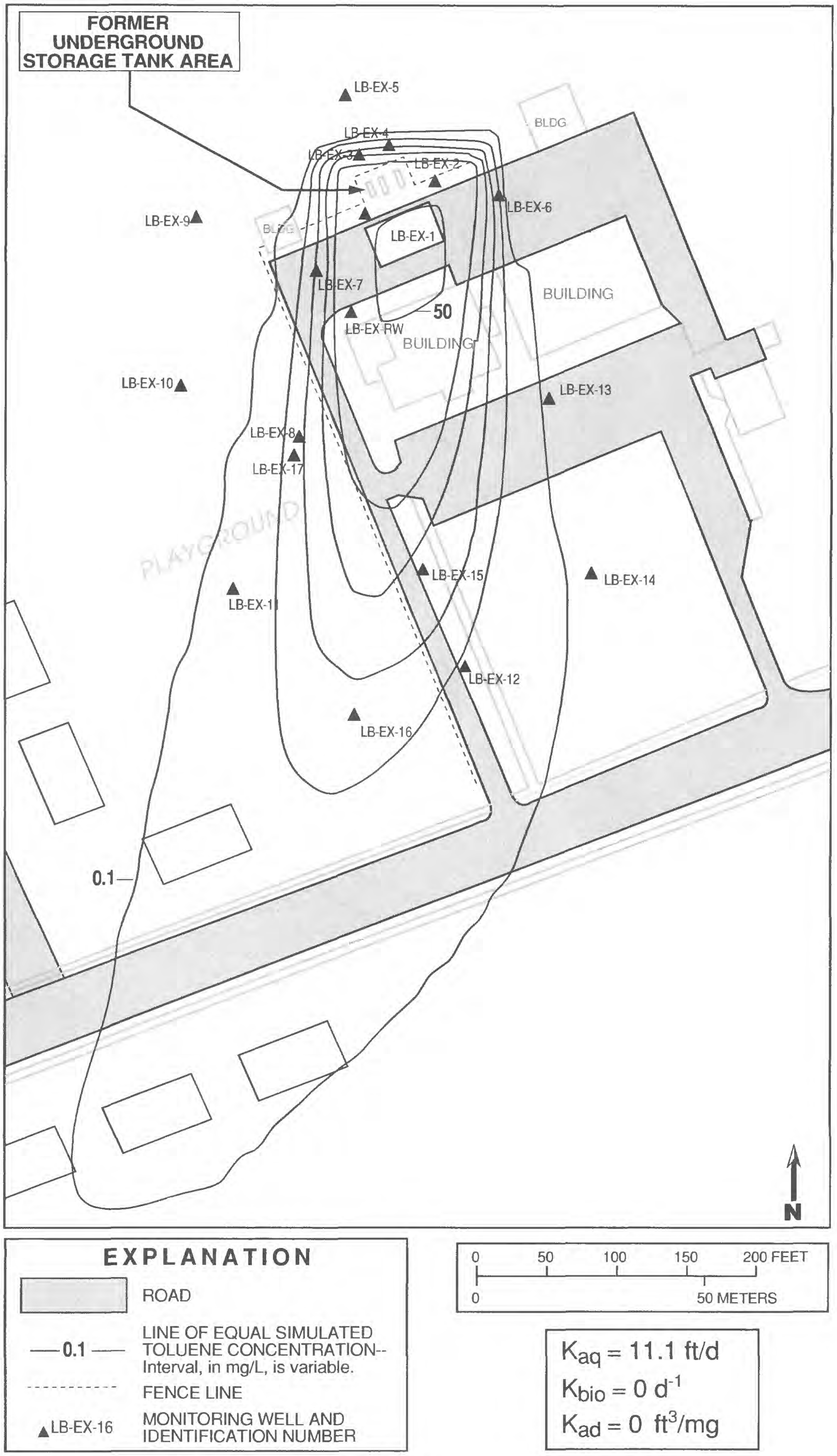


Figure 15. Simulated 1994 distribution of toluene released in 1991 assuming the Conservative Model at the Laurel Bay Exchange, Marine Corps Air Station Beaufort, S.C.

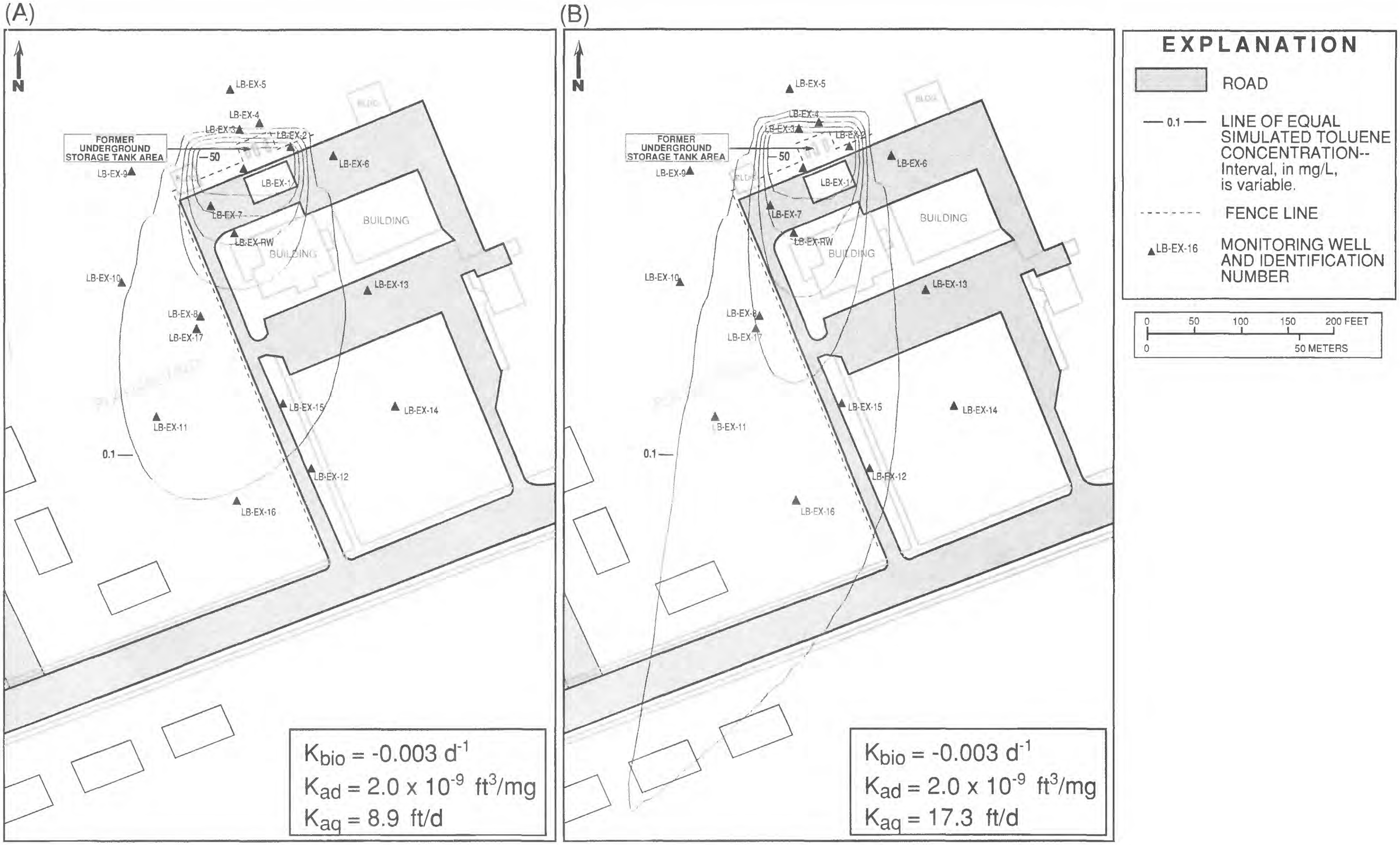


Figure 16. Simulated 1994 distribution of toluene for (A) minimum and (B) maximum values of hydraulic conductivity at Laurel Bay Exchange, Marine Corps Air Station Beaufort, S.C.

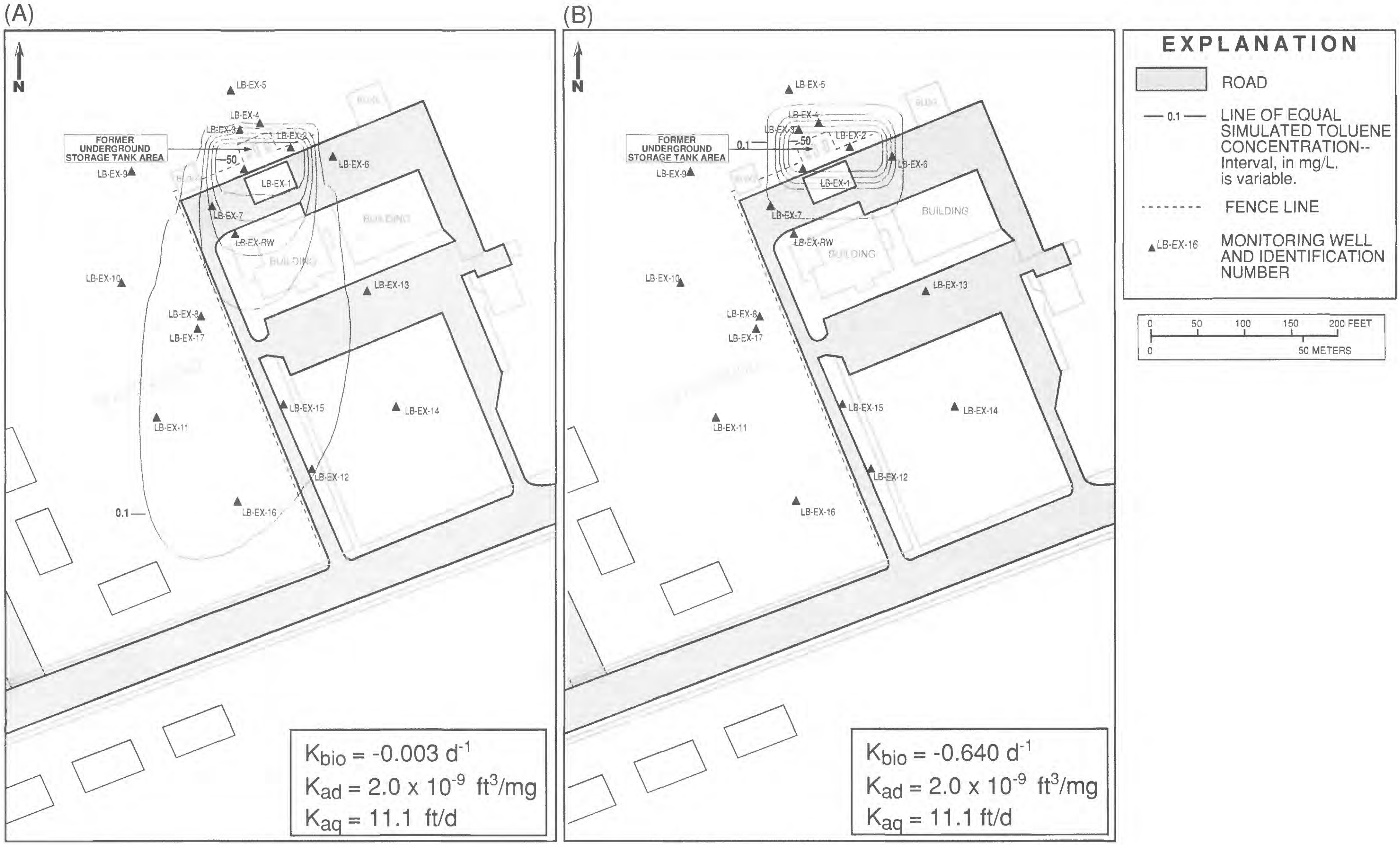


Figure 17. Simulated 1994 distribution of toluene for (A) minimum and (B) maximum values of biodegradation at Laurel Bay Exchange, Marine Corps Air Station Beaufort, S.C.

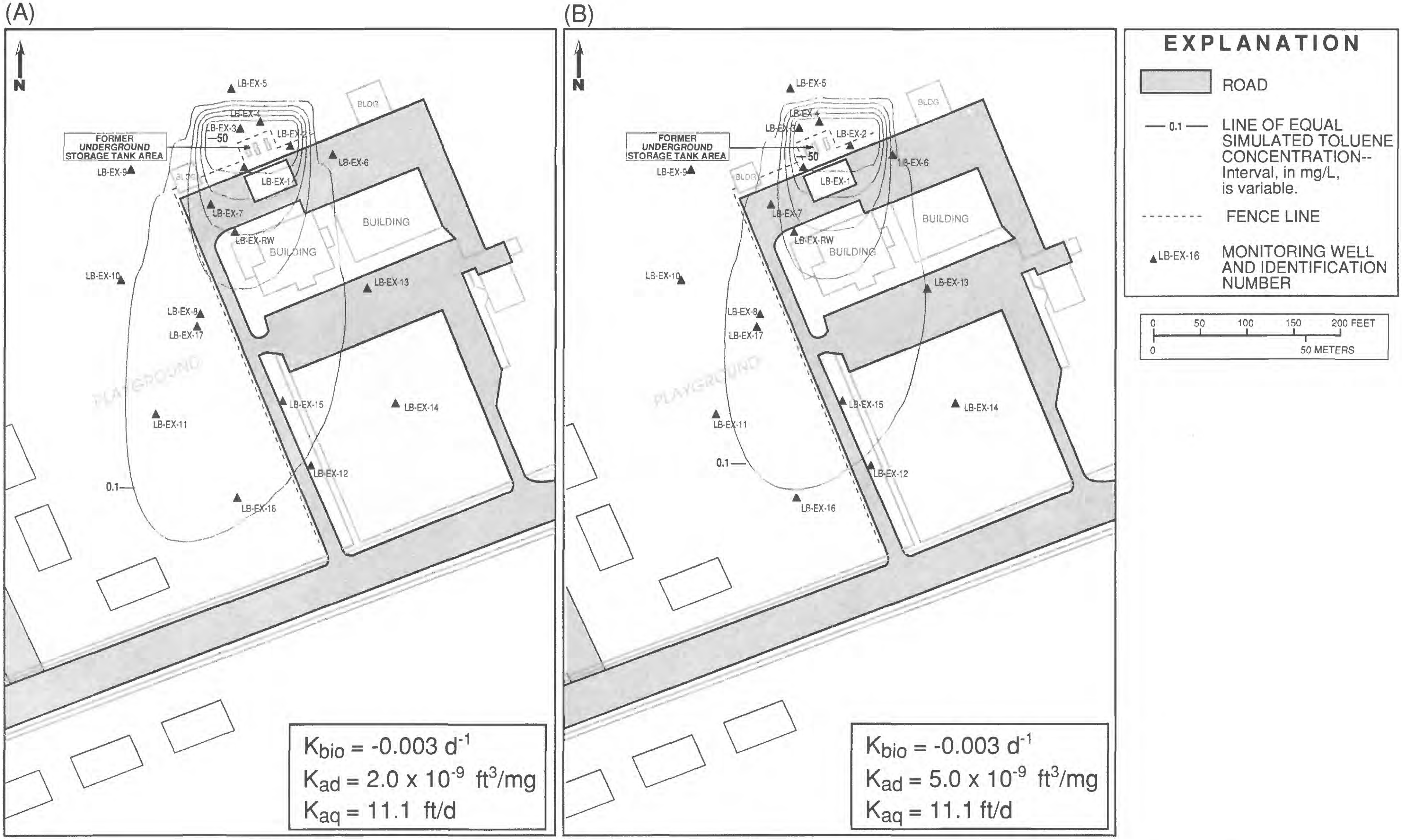


Figure 18. Simulated 1994 distribution of toluene for (A) minimum and (B) maximum values of toluene adsorption capacity at Laurel Bay Exchange, Marine Corps Air Station Beaufort, S.C.

The model analyses indicate that toluene concentrations at Laurel Bay are sensitive to the aquifer hydraulic conductivity (K_{aq}) and biodegradation rate (K_{bio}), and relatively insensitive to adsorption (K_{ad}). To show extreme conditions, the 1994 distribution of toluene under the minimum and maximum values for all parameters was simulated (fig. 19A and B, respectively). Results suggest that the biodegradation rate increase (all uniformly aerobic) produces a greater affect (smaller plume) even though a high hydraulic conductivity is used. This suggests that inducing aerobic conditions at the site could significantly reduce toluene concentrations.

Removal of the contaminant source and its affect on toluene concentrations downgradient with time was simulated using the Standard Model for toluene (fig. 20A-E). Starting with the Standard Model plume of toluene, a source removal in 1994 was simulated. One year after the source is removed (1995), simulated toluene concentrations in the center of the plume decreased from 50 mg/L to about 5 mg/L (fig. 20A) and the center of the plume began to migrate to the south away from the old source area. Two years following source removal (1996), toluene concentrations again decreased by about 50 percent (fig. 20B). Plume size and length of transport was simulated for years 1998, 2000, and 2001 (fig. 20C-E, respectively). By 2001, toluene concentrations had reached about 0.1 mg/L.

Solute-Transport Simulations of Benzene Migration

The same approach used to develop and produce simulations of toluene migration was utilized to predict benzene migration. A Standard Model was constructed based on a set of most probable values (table 7). This model assumes that the water-table gradients remain constant with time (the water-level distribution is the same as of March 10, 1994), that the aquifer remains anaerobic and that the aquifer exhibits very little adsorption properties for benzene. As was the case for toluene transport simulations, this model is not intended to represent actual values of parameters, but rather to provide a standard against which to compare the results on solute transport from changing the parameters within the measured ranges.

Simulations of benzene distributions based on the Standard Model for 1993 (fig. 21) and 1994 (fig. 22) shows the development of a benzene plume from a constant source (free product leaching into ground water at 20 mg/L) introduced in late 1991. The model assumes the best estimate for hydraulic conductivity (K_{aq} = 11.1 ft/d), predominantly anaerobic rates of benzene degradation (K_{bio} = -0.00025 d^{-1}), and benzene adsorption (K_{ads} = 2.0 x 10^{-9} ft^3/mg). Ideally, the use of these parameters should approximate a simulated benzene plume migration similar to that observed during field sampling. A source removal in 1993 was necessary to simulate the 1994 benzene concentrations. In 1994, the simulated benzene plume (delineated by the 0.001 mg/L contour) reaches maximum dimensions of 400 ft, which is 50 ft farther than the 350 ft that the benzene plume migrated in the field (fig. 22). As was the case with simulated toluene concentrations, the difference can be explained by the lack of wells and available hydrocarbon data in areas the simulation depicts as being contaminated.

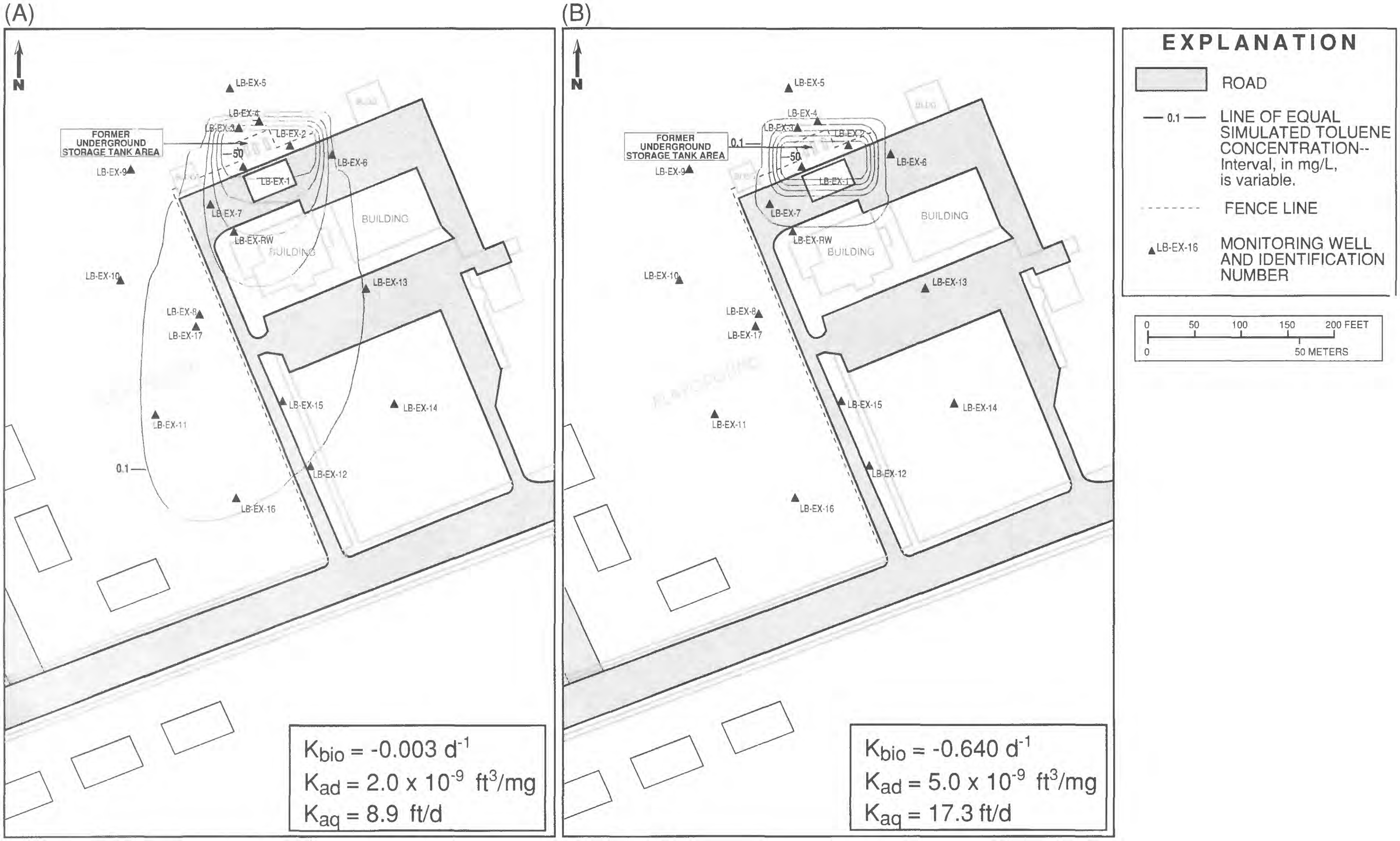


Figure 19. Simulated 1994 distribution of toluene for (A) minimum and (B) maximum values of hydrologic, geochemical, and microbial parameters at Laurel Bay Exchange, Marine Corps Air Station Beaufort, S.C.

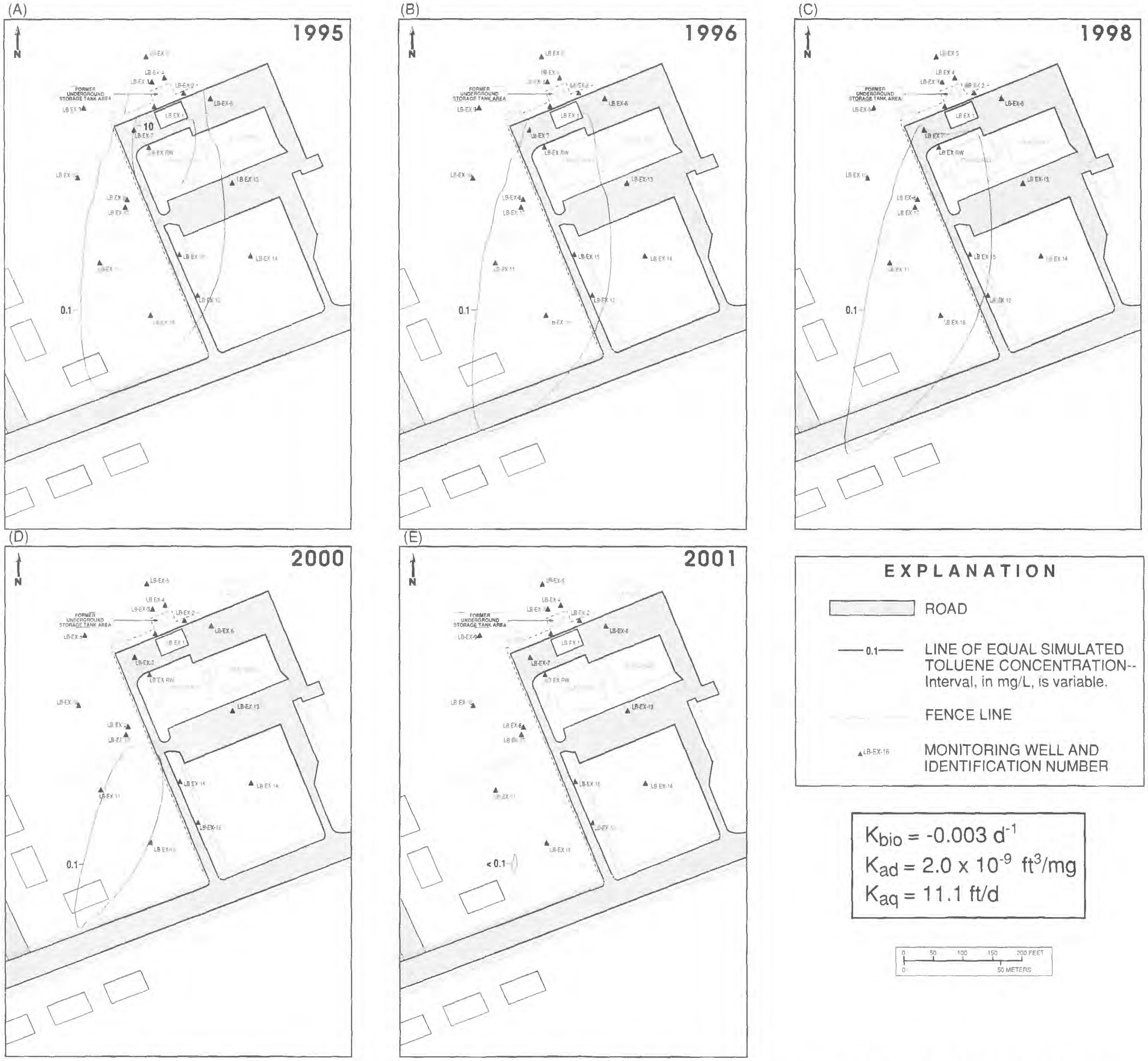


Figure 20. Simulated 1995 (A), 1996 (B), 1998 (C), 2000 (D), and 2001 (E) distribution of toluene after source removal in 1994, at Laurel Bay Exchange, Marine Corps Air Station Beaufort, S.C.

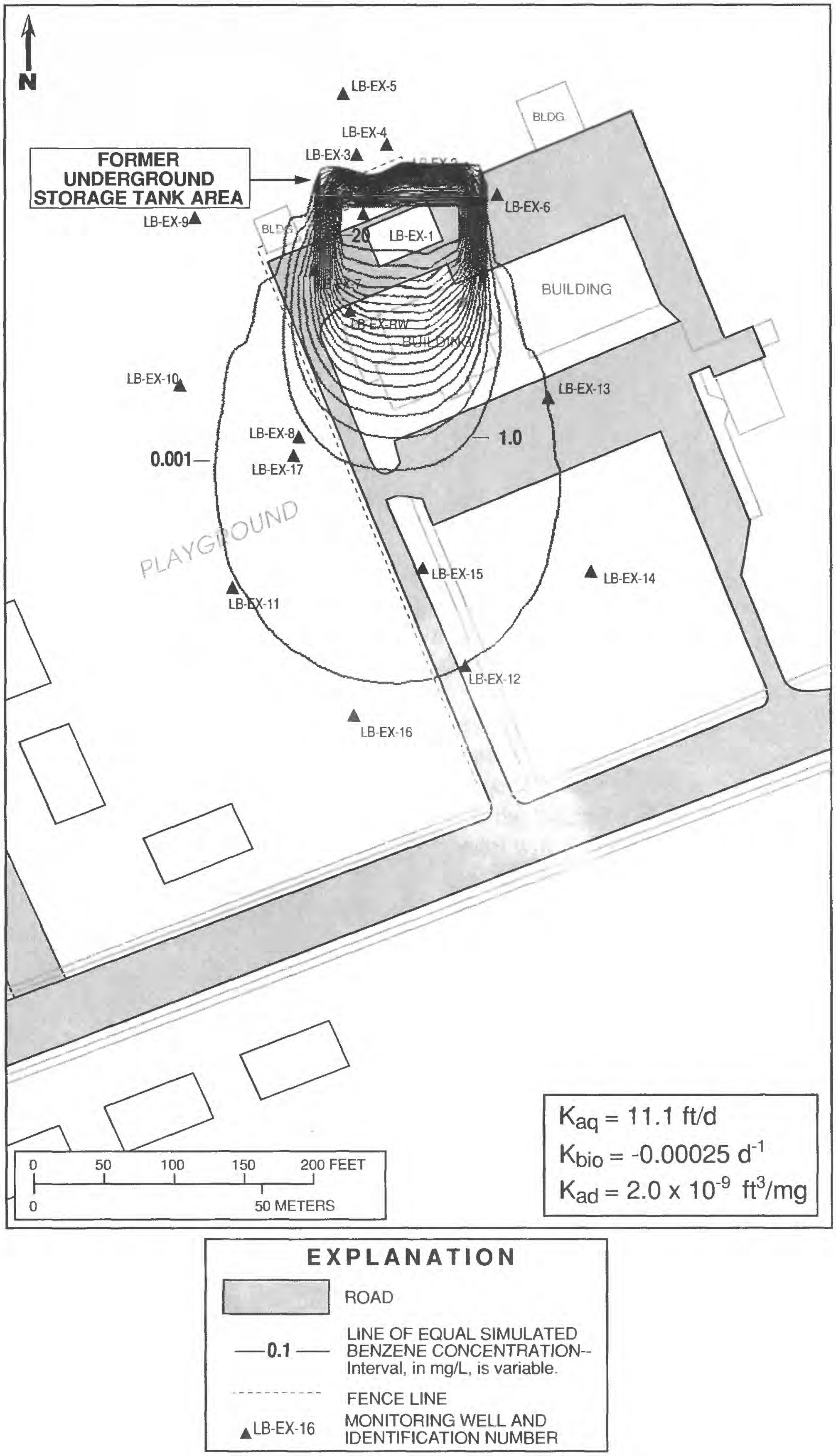


Figure 21. Simulated 1993 distribution of benzene for values of the Standard Model at Laurel Bay Exchange, Marine Corps Air Station Beaufort, S.C.

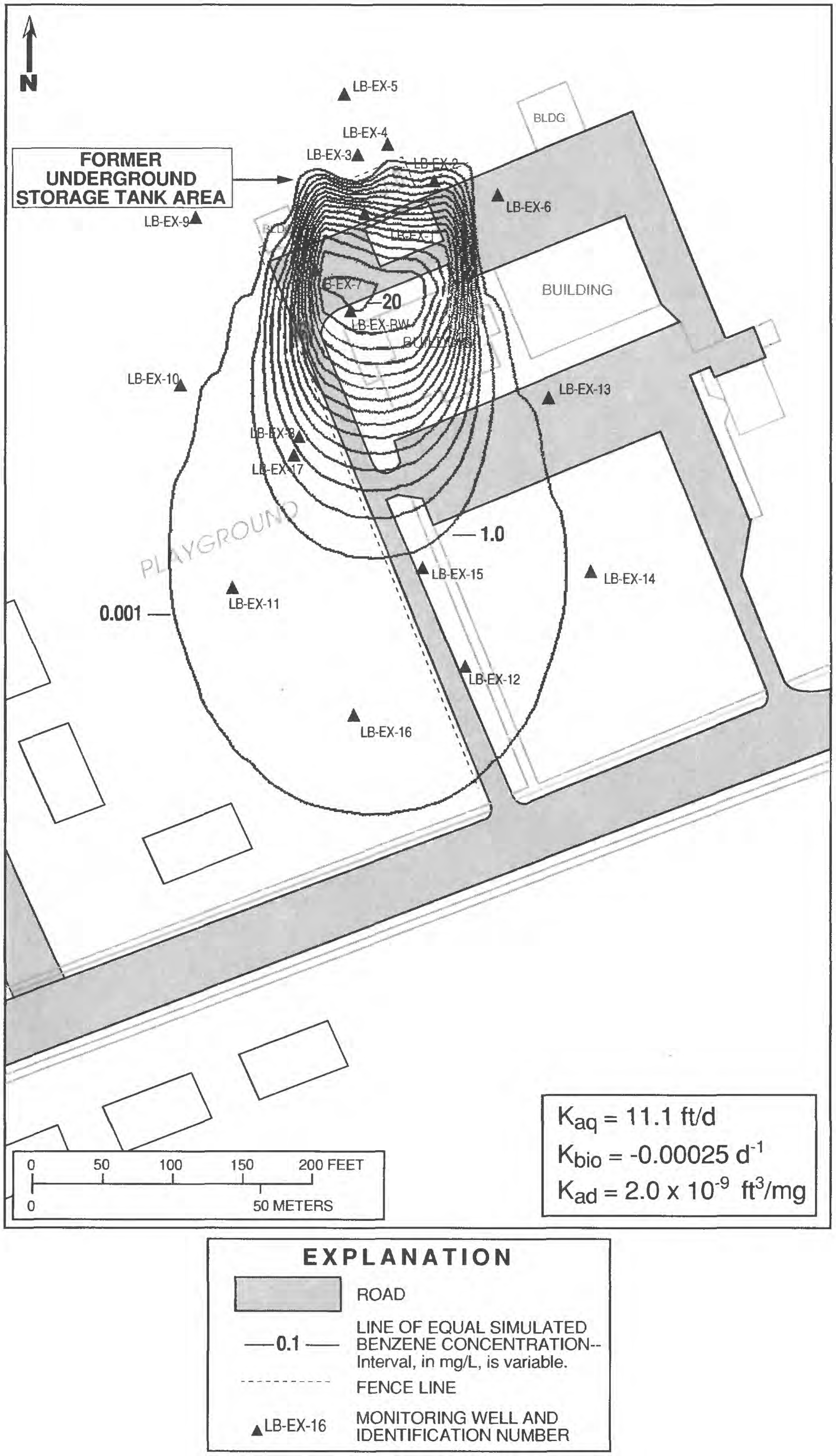


Figure 22. Simulated 1994 distribution of benzene for values of the Standard Model after source removal in 1993, at Laurel Bay Exchange, Marine Corps Air Station Beaufort, S.C.

Simulations for the Standard Model were run until the year 2044 (fig. 23A-C). The contaminants do not migrate to the nearest POC 2,400 ft south of the site boundary by the year 2044.

The worst-case benzene-transport scenario, a conservative model, of no biodegradation and no adsorption was simulated (fig. 24A). Because there is no retardation of the contaminant by either adsorption or biodegradation, the plume migrates with the rate of the ground-water velocity. The benzene plume migrates farther than that predicted by simple advection, as a result of the dispersive effects of the fine sand grains in the aquifer that cause some ground-water flowpaths to be longer. The extent of the plume (delineated by the isoconcentration line of 0.001 mg/L (fig. 24A-C) has migrated about 470 ft from the source area by 1994 since release in 1991. A transport rate of about 157 ft/yr can be calculated, which simulates some level of benzene in the POC in about 23 years. The Conservative Model also indicates that the plume does not enlarge continuously over time, as in the case of toluene, because the source of dissolved benzene had been removed. Hence, benzene concentrations decrease because of dilution with ground water.

The effects of hydraulic conductivity on simulated plume migration were determined using the Standard Model. Distributions of benzene using uniformly low (K_{aq} = 8.9 ft/d) and high (K_{aq} = 17.3 ft/d) hydraulic conductivities were simulated for the years 1994 and 2022 (figs. 25A and B and 26A and B, respectively). From a comparison of the plume dimensions, the higher hydraulic conductivity results in a larger plume by about 150 ft in length because of a higher rate of ground-water flow.

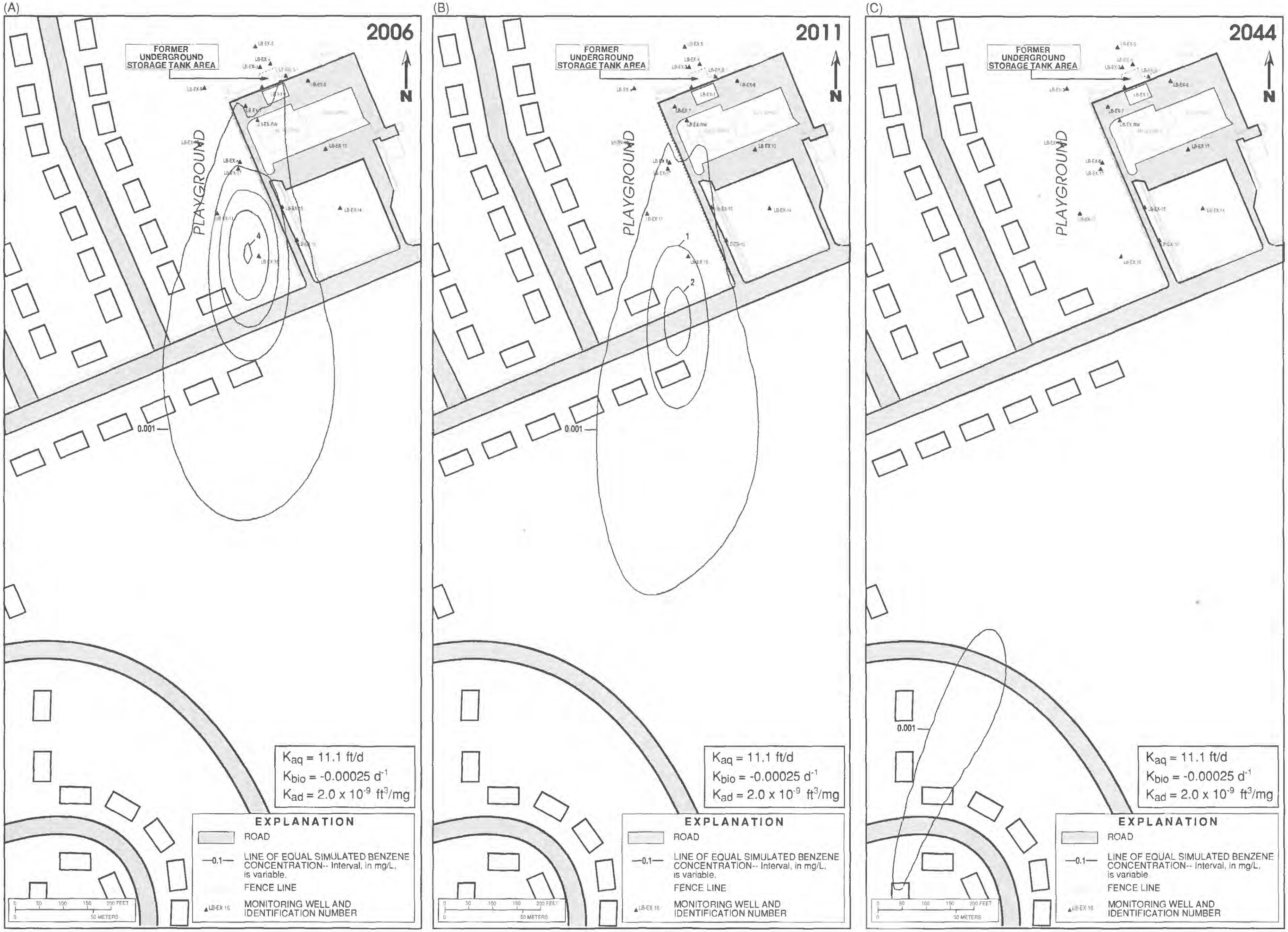


Figure 23. Simulated 2006 (A), 2011 (B), and 2044 (C), distributions of benzene assuming Standard Model transport parameters, at Laurel Bay Exchange, Marine Corps Air Station Beaufort, S.C.

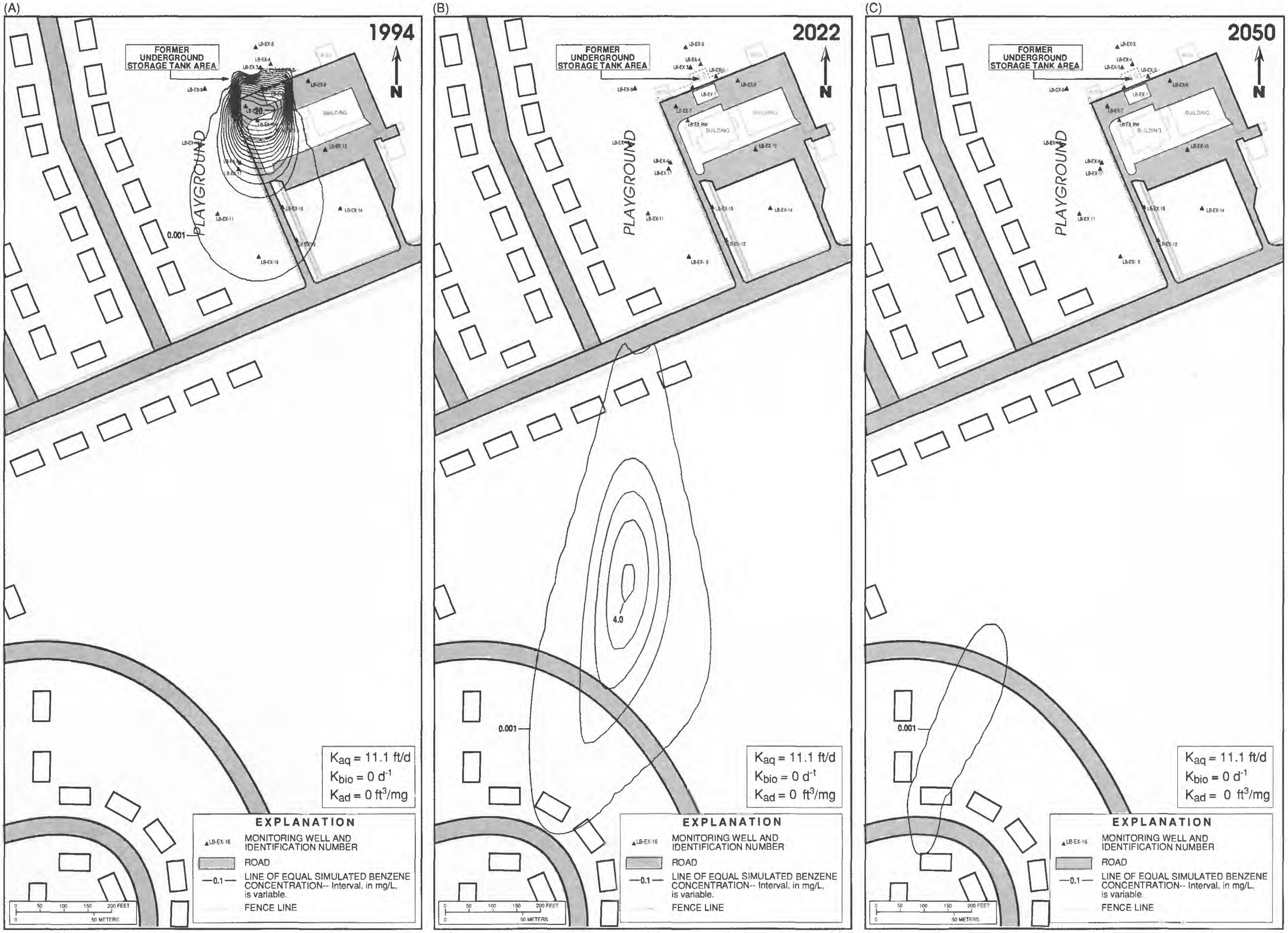


Figure 24. Simulated 1994 (A), 2022 (B), and 2050 (C) distributions of benzene assuming Conservative Model transport, at Laurel Bay Exchange, Marine Corps Air Station Beaufort, S.C.

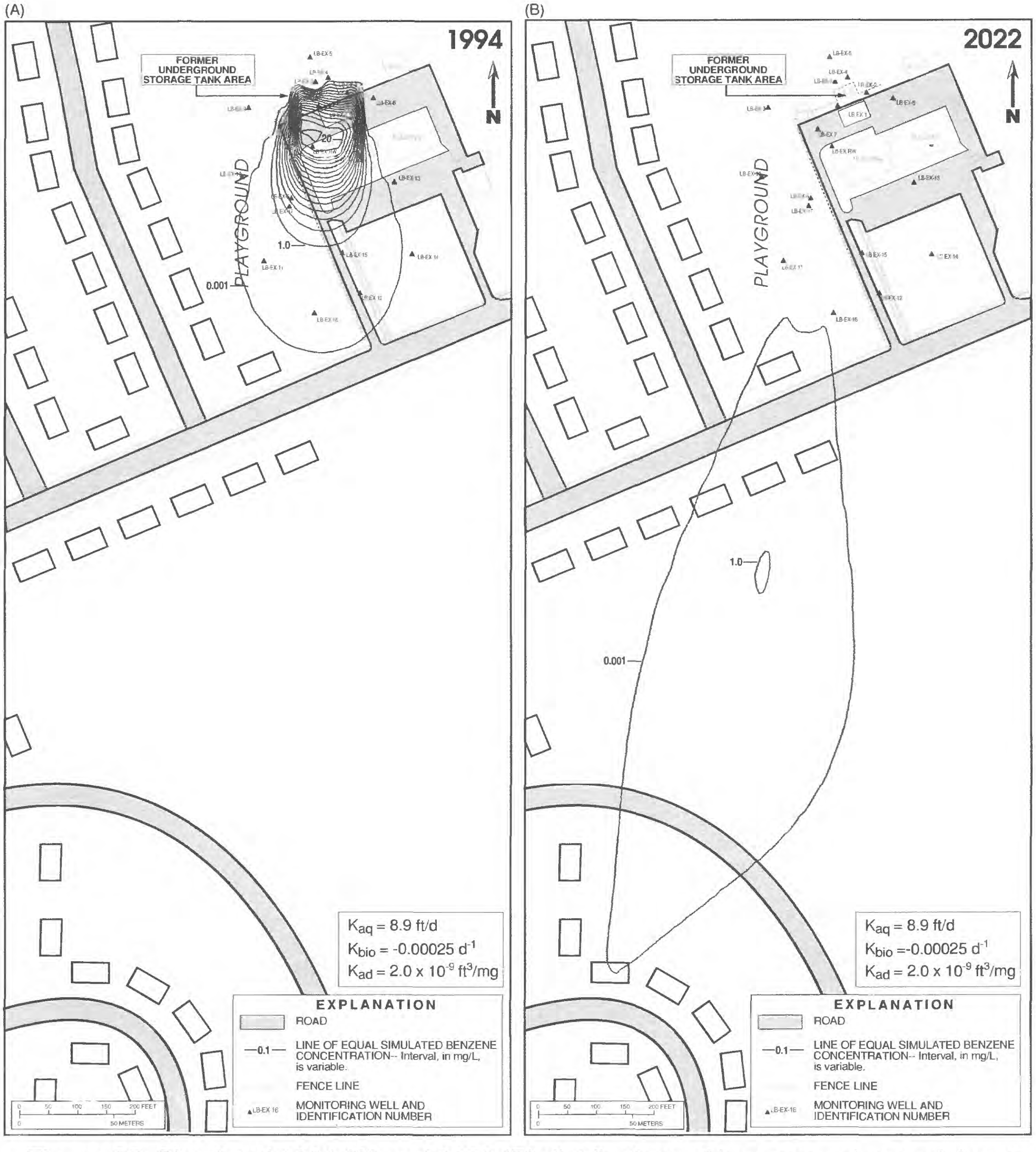


Figure 25. Simulated 1994 (A) and 2022 (B) distributions of benzene using a minimum value of hydraulic conductivity, at Laurel Bay Exchange, Marine Corps Air Station Beaufort, S.C.

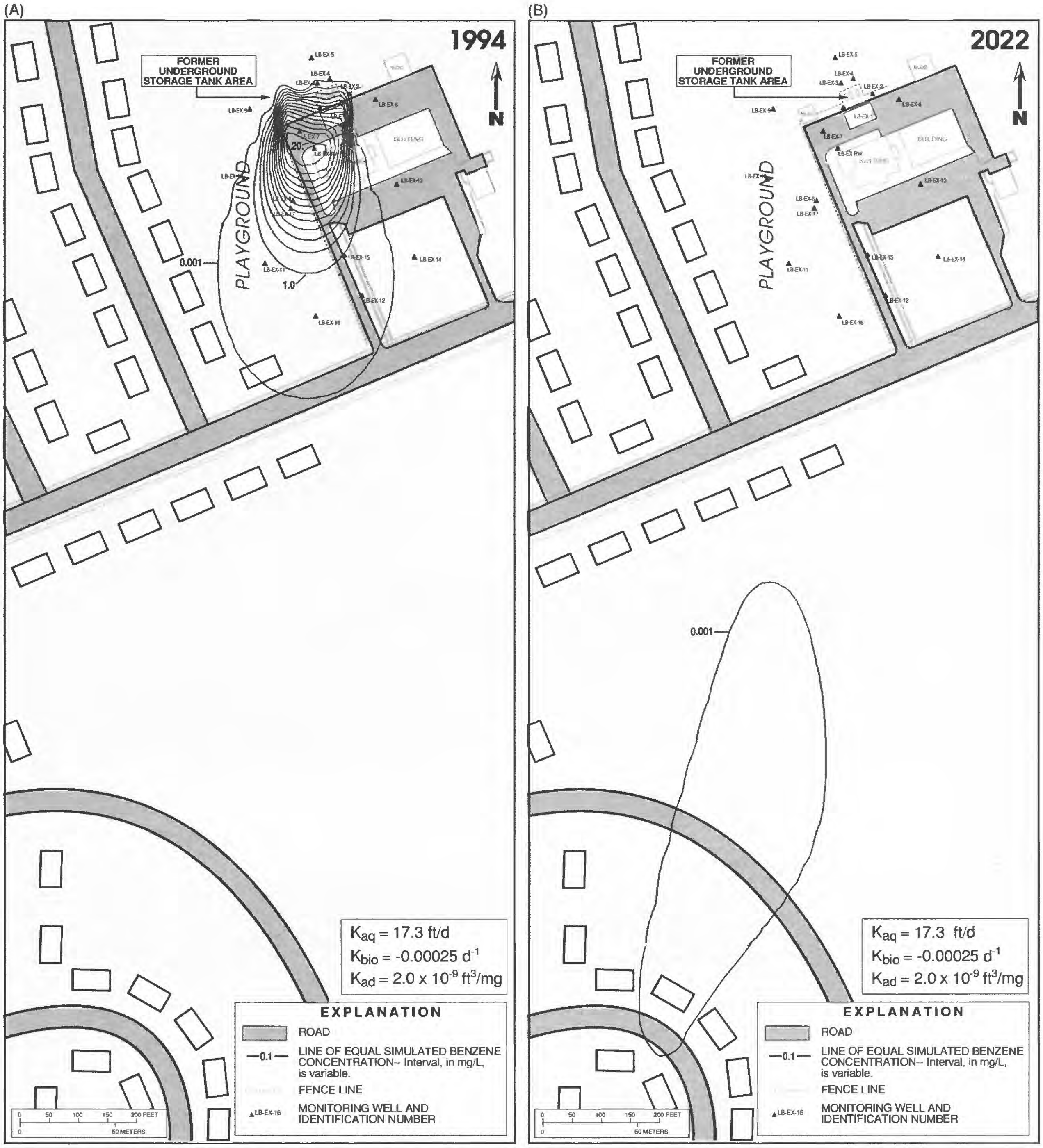


Figure 26. Simulated 1994 (A) and 2022 (B) distributions of benzene using a maximum value of hydraulic conductivity, at Laurel Bay Exchange, Marine Corps Air Station Beaufort, S.C.

CONCLUSIONS

Exploratory modeling simulations indicate that there is no combination of reasonable ranges of known hydrologic, geochemical, or microbial conditions, as determined at the sites, that could result in petroleum-hydrocarbon contaminant transport to a point-of-contact with humans or wildlife at the Laurel Bay Exchange. It appears that contaminants are effectively isolated under current site conditions, that they are not affecting adjacent surface-water bodies, nor are they likely to in the future. This, in turn, suggests that intrinsic bioremediation is a possible remedial option for containing contaminated ground water at Laurel Bay. Available evidence indicates that removal of free product- or sorption-contaminated sediments can accelerate the intrinsic bioremediation of contaminated ground water at the site.

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