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UCRL-AR-125619

Assessment of Appropriate Fuel Hydrocarbon Risk-Management Strategies for George Air Force Base, Victorville, California Using a Risk-Based Approach

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January 1997

Submitted to the Air Force Center for Environmental Excellence
Environmental Restoration Directorate
Technology Transfer Division, Brooks Air Force Base, Texas

*Environ Corporation, Emeryville, California
**Arizona State University, Tempe
***University of California, Santa Barbara
****University of California, Berkeley

Environmental Protection Department
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Work performed under the auspices of the U. S. Department of Energy by Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

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Acknowledgments

This study is part of the DoD Petroleum Hydrocarbon Demonstration Program (PHCDP). Funding for this work was provided by the U.S. Air Force Center for Environmental Excellence (AFCEE), Environmental Restoration Directorate, Technology Transfer Division (ERT) at Brooks Air Force Base, Texas. Marty Faile, Division Chief, and Patrick Haas, AFCEE/ERT Point of Contact, have been very supportive, and have provided the necessary Air Force guidance and backing for this effort. Charles Lee, of the AFCEE Regional Compliance Office in San Francisco, has been the champion of this effort within the military community, and has worked tirelessly to create and sustain this Program. His Risk Execution Strategy for Clean-Up of the Environment (RESCUE) has been the guiding vision for PHCDP and the LUFT demonstrations at military bases in California..

A number of dedicated individuals have contributed to the preparation of this report. The authors would like to thank the following individuals for their dedication, expertise, and hard work:

H. Barnes

L. Berg

D. Bishop

K. Brown

R. Depue

C. Kuks

R. Ragaini

J. Wharton

1. Program Overview

1.1. Background

In June 1994, the State Water Resource Control Board (SWRCB) contracted with the Lawrence Livermore National Laboratory/ University of California (LLNL/UC) Leaking Underground Fuel Tank (LUFT) Team to study the cleanup of LUFTs in California. The study consisted of data collection and analysis from LUFT cases and a review of other studies on LUFT cleanups. Two final reports were submitted to the SWRCB in October and November 1995. These reports were entitled: *Recommendations To Improve the Cleanup Process for California's Leaking Underground Fuel Tanks (LUFTs)*, and *California Leaking Underground Fuel Tank (LUFT) Historical Case Analysis*.

Prior to submittal, both LLNL/UC reports were subjected to extensive internal peer review within the LLNL, as well as within each of the four UC campuses involved: UC Berkeley, UC Santa Barbara, UC Davis, and UC Los Angeles. The U.S. Environmental Protection Agency (EPA) has reviewed both LLNL/UC reports and issued a fact sheet supporting the findings and recommendations. Both reports have received national attention and have been extensively reviewed by many interested parties.

Data were collected primarily from the alluvial geologic settings typical of the San Francisco Bay Area, Los Angeles Basin, and the Central Valley. These data represent California's highly populated areas where most gas stations are found and most LUFT releases occur. Study results can be applied to similar settings throughout California. The length of dissolved benzene plumes in groundwater at LUFT releases were evaluated over time to determine how plumes behave. Over 1,200 LUFT cases were evaluated. Benzene was analyzed because it is the human carcinogen of greatest concern in fuel. It is relatively soluble in water, and cleanup standards are generally tied to benzene concentrations.

Ninety percent of the dissolved benzene plumes were less than 260 ft in length. Most of these plumes were either stable or shrinking in length. Seventy percent of the plumes in the study sites were found in shallow groundwater, less than 25 ft below the ground surface.

1.1.1. The Use of Natural Attenuation

The study concluded that with rare exceptions, petroleum fuel releases will naturally degrade (passively bioremediate) in California's subsurface environments. Passive bioremediation can control groundwater contamination in two distinct ways. First, passive bioremediation substantially lowers the risk posed to downgradient risk receptors through plume stabilization[1]. Second, passive bioremediation actively destroys fuel hydrocarbon mass in the subsurface, leading to remediation of contamination over time (i.e., eventual decline and depletion of the dissolved hydrocarbon plume). From a risk-management viewpoint, the stabilization of the dissolved plume is the most important contribution of passive bioremediation.

The use of passive bioremediation still requires site characterization and an assessment of potential risks. The need for active source removal must also be addressed on a site-by-site basis. Source removal includes removing leaking tanks and lines, and removing free product and

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[1] Even in the presence of a continuous constant source of fuel hydrocarbons (e.g., dissolution of residual free product components trapped in the soil matrix), a groundwater plume subject to passive bioremediation will reach a steady-state condition in which plume length becomes stable. This will occur when the rate of hydrocarbon influx from dissolution of the residual free product source is balanced by the rate of mass loss via passive bioremediation, integrated across the entire spatial extent of the plume.

petroleum fuel saturated soil, as much as economically and technically feasible. Although active source removal will contribute to higher rates of contaminant remediation in some instances, it will not diminish the risk posed to downgradient risk receptors by a plume which has already stabilized as a result of passive biodegradation.

The role of passive bioremediation in controlling the behavior of dissolved hydrocarbon plumes may be evaluated through both primary and secondary field evidence. Primary evidence includes quantitative evaluation of plume stability or plume shrinkage based upon trends in historical groundwater data. Secondary evidence includes indirect indicators of passive bioremediation, such as variations in key geochemical parameters (dissolved oxygen, nitrate, sulfate, iron, manganese, methane, alkalinity/carbon dioxide, Eh, pH) between measurements in fuel hydrocarbon-impacted areas and background. Although primary evidence of plume stability or decline generally provides the strongest arguments to support natural attenuation at a given site, such evidence may not be available because adequate historical groundwater monitoring may not exist. In these cases, short-term monitoring data, in conjunction with modeling where appropriate, may support a hypothesis for the occurrence of passive bioremediation if supported by secondary lines of evidence. Consequently, means for assessing the role of natural attenuation in controlling risk by secondary lines of evidence are to be more fully explored at such sites.

1.2.1. Risk-Based Corrective Action

The LLNL/UC recommendations report also concluded that risk-based corrective action (RBCA) provides a framework to link cleanup decisions to risk. For a risk to exist, there must be a source of a hazard, a receptor, and a pathway that connects the two. All three factors must be addressed to determine whether a LUFT release poses a risk to human health, safety, or the environment. If the source, pathway, or receptor are at all times absent, there is, by definition, no risk. The distinction between sources, pathways, and receptors may be context-dependent in many cases and therefore must be carefully defined. For purposes of the present assessment, definitions of these terms are developed by working backward from the receptor to the source:

Receptor: Human or ecological risk receptors which may potentially be subject to damage by long-term exposure to hydrocarbons via ingestion, inhalation, or absorption. This definition also specifically includes water supply wells because it must be assumed that humans will be ingesting the water from these wells.

Pathways: Physical migration routes of contaminants from sources to risk receptors. This definition specifically includes the groundwater environment downgradient of the source which provides a medium through which dissolved contaminants may migrate to water supply wells, as well as to surface water bodies which may serve as ecological risk receptors. The definition also includes the vadose zone in the immediate vicinity of the source, where vapor migration routes to nearby human receptors may exist.

Sources: Points of entry of contaminants into possible exposure pathways. In the case of hydrocarbon releases associated with LUFT sites, separate-phase hydrocarbon product which can either dissolve into the aqueous phase or volatilize into the gaseous phase constitutes a source. Primary sources will include underground tanks and associated piping; secondary sources will include any separate-phase hydrocarbon free product material residing within sediment pores.

From a mathematical viewpoint, sources and receptors represent boundary conditions for the problem of interest (influx and outflux, respectively); pathways represent the problem domain. Thus, in some special situations, the dissolved plume in groundwater may represent a source, such as in the case of Henry’s law partitioning of contaminants from the aqueous phase into the gaseous phase. On the other hand, hydrocarbons which have adsorbed onto sediment surfaces from the aqueous phase cannot be regarded as potential sources in most situations according to this definition, but rather exist as part of the pathway.

Risk characterization is defined as an information synthesis and summary about a potentially hazardous situation that addresses the needs and interests of decision makers and of interested and affected parties. Risk characterization is a prelude to cleanup decision making and depends on an iterative, analytic, and deliberative process. This process attempts to gather all relevant data so the decision makers may then choose the best risk-management approach. If the risk of affecting receptors (humans or ecosystems) is low, then the following risk-management strategy is appropriate and cost effective: 1) perform primary source removal (i.e., remove and upgrade leaking underground tanks and lines) and, 2) use passive bioremediation at low-risk sites, supported by monitoring as appropriate.

1.2. LUFT Demonstration Program

One of the important recommendations of this study was to identify a series of LUFT demonstration sites and to form a panel of experts made up of scientific professionals from universities, private industry, and Federal and State regulatory agencies. This panel would provide professional interpretations and recommendations regarding LUFT evaluations and closures at demonstration sites.

As a result of this recommendation, ten Department of Defense (DoD) sites were selected. Site selection was coordinated through the California Military Environmental Coordination Committee (CMECC) Water Process Action Team (PAT). Sites were selected to represent each branch of the military services with bases in California, as well as a number of Regional Water Quality Control Boards (RWQCB) and the diverse hydrogeologic settings in California where fuel hydrocarbon contaminant (FHC) cleanup problems occur. The sites selected and their corresponding RWQCB region are:

- Army Presidio at San Francisco, San Francisco RWQCB.
- Barstow Marine Corps Logistic Center, Lahontan RWQCB.
- Camp Pendleton Marine Corps Base, San Diego RWQCB.
- Castle Air Force Base, Central Valley RWQCB.
- China Lake Naval Weapons Center, Lahontan RWQCB.
- El Toro Marine Corps Air Station, Santa Ana RWQCB.
- George Air Force Base, Lahontan RWQCB.
- Port Hueneme Naval Construction Battalion Center, Los Angeles RWQCB.
- Travis Air Force Base, San Francisco RWQCB.
- Vandenberg Air Force Base, Central Coast RWQCB.

The Expert Committee (EC) selected to evaluate the selected demonstration sites are:

- Mr. David W. Rice, LLNL, Environmental Scientist; Project Director SWRCB LUFT Re-evaluation Project; LLNL/UC LUFT Team member; DoD FHC Demonstration Program Coordinator.
- Dr. Walt McNab, LLNL, Hydrogeochemist, with expertise in the evaluation of passive bioremediation processes.
- Dr. William E. Kastenberg, UC, Berkeley, Professor and Chairman, Department of Nuclear Engineering; member of LLNL/UC LUFT Team, with expertise in environmental decision making and decision analysis processes.

- Dr. Lorne Everett, UC, Santa Barbara, Hydrogeologist; head of the Vadose Zone Research Laboratory and member of LLNL/UC LUFT Team, with expertise in vadose zone FHC transport mechanisms and passive bioremediation processes.
- Dr. Stephen Cullen, UC, Santa Barbara, Hydrogeologist; member of LLNL/UC LUFT Team with expertise in vadose zone FHC transport mechanisms and passive bioremediation processes.
- Dr. Paul Johnson, Arizona State University, Chemical Engineer; primary author of *American Society for Testing and Materials (ASTM) RBCA* guidance, with expertise in chemical fate and transport.
- Dr. Michael Kavanaugh, Chairman, National Research Council Alternatives for Groundwater Cleanup Committee; Environmental Engineer, Environ Corporation, with expertise in evaluation of groundwater remediation alternatives and environmental decision making processes.

The demonstration program process can be summarized in the following nine steps:

1. Site scoping meeting with site staff, regulators, and EC staff representatives. Develop and discuss site conceptual model. Identify and discuss pathways and receptors of concern.
2. RBCA training for DoD Petroleum Hydrocarbon Cleanup Demonstration Program (PHCDP) participants.
3. Site staff and contractors prepare the data package. EC staff reviews available data and identifies data gaps needed to apply RBCA approach.
4. EC visits site and receives briefing, on site characterization, conceptual model, and pathways and receptors of concern. Site tour is included in this briefing. Following EC's visit, a site characterization report is prepared by the EC containing recommendations for further data collection, if needed.
5. EC staff applies RBCA approach to the site using best available data.
6. EC staff evaluates the natural attenuation potential for the site using best available data. An estimate of the time to clean up and the uncertainty associated with this estimate will be made. Sampling and monitoring procedures to support intrinsic bioremediation for the site will be identified.
7. Based on the concept of applied source, pathways, and receptors as to potential hazards, site specific findings regarding natural attenuation potential, and discussion with regulators, the EC shall provide its recommendations for an appropriate risk-management strategy at the site and the set of actions needed to achieve site closure. The EC will present its recommendations at an appropriate forum.
8. The EC will provide a DoD PHCDP overall evaluation comparing the effectiveness of CalRBCA at each site in the program. An estimation of the cost savings using the CalRBCA protocol will be compared to baseline approaches. An estimation of the value of the remediated water will be made.

9. The EC Staff will produce a DoD *Risk Execution Strategy for Clean-Up* of the Environment (RESCUE) implementation guide and accompanying procedures manual (Phase I, Petroleum) that can be used in California and in other states by military bases.

2. Site Overview

2.1. Background

George Air Force Base (GAFB) is located in Victorville, California. The base was active until 1992 when it was closed as part of the base realignments and closures approved by the Secretary of Defense and Congress. It is anticipated that GAFB will eventually be used as a regional international airport. The base facilities are intended to house a variety of small businesses and light industry.

Petroleum hydrocarbons (originally JP-4 aviation fuel) are in the subsurface environment at GAFB as a result of leaks from underground tanks and piping systems. A significant volume of free product, estimated to be on the order of 350,000 gal, resides on top of the water table, covering an area of approximately 32 acres, with product thickness ranging from a thin sheen to several feet. A plume of dissolved FHCs exists in the underlying groundwater, extending several hundred feet downgradient of the free product lens. Isolated pockets of low concentrations of dissolved halogenated hydrocarbons (trichloroethylene [TCE], tetrachloroethylene [PCE], dichloroethane [1,1-DCA]) have also been noted in site groundwater.

GAFB Operable Unit #2 (OU#2) was selected as a site for the Demonstration Program because the base has collected a considerable amount of data and has established technical protocols that would be valuable in evaluating the recommendations proposed by the LLNL/UC report. Extensive remedial investigations and risk assessments have been performed according to EPA's *Risk Assessment Guidance for Superfund - Human Health Evaluation Manual* and were available for review. The petroleum hydrocarbon compounds benzene, toluene, ethylbenzene, and xylenes (BTEX) associated with OU#2 were identified as chemicals of concern.

2.2. Site Conceptual Model

The site is underlain by alluvial sediments consisting of unconsolidated sand, silt, clay, and gravel in an arid climatic setting. A perched unconfined aquifer extends from a depth of about 125 to 196 ft below ground surface and is perched on a 20-ft-thick aquiclude of clay and clayey silt. Below the perched aquifer is a second vadose zone (unsaturated zone) extending to a deeper aquifer at a depth of 268 ft. The aquiclude is continuous from exposures southeast of the base to north of OU#2.

Hydraulic conductivity values have been calculated from a number of pumping and aquifer tests (although analyses associated with the two methods have produced estimated values that are not entirely self-consistent). When interpolated hydraulic head values and porosity estimates are considered, these data suggest groundwater movement in a north-northeasterly direction at a rate of tens to hundreds of feet per year[2]. Little recharge/evapotranspiration is expected in association with the unconfined aquifer.

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[2] Zones of relatively high hydraulic conductivity have been identified in downhole flow meter tests (Wilson et al., 1996). However, such zones appear to be on the order of only one or two feet in thickness and probably do not extend over site-wide scales of observation.

The spatial extent of the dissolved FHC constituents/BTEX in groundwater appears reasonably well-characterized over individual sampling rounds, although long-term historical trends in individual wells are not available. Concentrations of natural attenuation geochemical indicator species (e.g., dissolved oxygen, nitrate, sulfate, iron, methane, redox potential) have also been collected from 16 monitoring wells as part of a natural attenuation monitoring study. Evidence has been presented indicating passive bioremediation processes are occurring at GAFB. These include apparent shrinkage of BTEX constituent plumes with time, loss of BTEX components in comparison to recalcitrant dissolved FHC constituents (trimethylbenzene isomers), and changes in geochemical indicator species which vary in space in a manner consistent with expected passive bioremediation.

A review of the adequacy of the site conceptual model was presented to GAFB in a letter dated July 30, 1996 (Appendix A).

3. Risk Analyses and Management

3.1. Sources

3.1.1. Primary Source(s)

Petroleum hydrocarbons (originally JP-4 aviation fuel) are in the subsurface environment at GAFB as a result of leaks from underground tanks and piping systems. Vadose zone contamination encountered during drilling and soil analyses indicate that there were two primary sources for the free product plume: Fuel Pit 1 and Fuel Pit 3/Main Pump Station area located in the flight-line aircraft parking apron. The original liquid fuel-supply system, constructed of 3- to 6-in. aluminum pipes, leaked an unknown volume during the early 1970s. Four 50,000-gal underground storage tanks (USTs) were taken out of service in 1990 after failing two consecutive leak tests. The rates and quantities of leakage are unknown. The USTs were removed along with contaminated soils and disposed of.

3.1.2. Secondary Source(s)

A significant volume of free phase product, estimated on the order of 350,000 gal, persists on top of the perched aquifer water table. This free product covers an area of approximately 32 acres, with free product thickness ranging from a thin sheen to several feet. The free product plume appears to flow to the northwest from release areas under the flight-line aircraft parking apron. Movement of the free product is slowed and possibly stopped by the fine-grained deposits within buried stream channels. No contamination has been detected in groundwater samples taken from the deep aquifer beneath OU#2.

The mobile components of the JP-4 aviation fuel secondary sources (e.g., BTEX compounds and the light aromatic hydrocarbons, short-chained alkanes) will have migrated the farthest before the plume is stabilized. Long-chain, less water-soluble and less volatile components will be largely confined to the limited regions of the subsurface where the free product has resided. As natural weathering of the free product occurs through volatilization and dissolution, secondary sources will become depleted in the mobile compounds and the long-chain fuel components will remain. These compounds do not dissolve readily in water and their extent will most likely be limited by the original extent of the free product. Fortunately, the long-chain hydrocarbons are relatively non-toxic and can be expected to have little impact on taste or odor beyond the immediate area of free product impact.

3.1.3. Engineered Source Removal

Current active source remediation techniques in use, or under consideration, at GAFB include free product removal and capillary fringe bioventing. Free product remediation consists of mobile and permanent free product recovery systems, which remove approximately 160 gal of free product per day, with a cumulative total of approximately 32,000 gal to date. The bioventing program has to date consisted largely of a treatability test.

Experience suggests that free product removal tends to be less successful the longer the time since the release. Based on current free product volume estimates, the current mass removed represents approximately 10 percent of the estimated free product source mass. For new releases, free product removal volumes between 70 percent and 90 percent are possible, depending on the geological conditions at the site. However, this percentage quickly declines as the free product spreads, becoming trapped by capillary forces in the pore spaces and isolated as distinct ganglia. Free product removals of up to 30 percent are much more typical.

3.1.4. Passive Source Removal By Natural Dissipation Processes

To address the time required for the free product lens to dissolve (coupled with passive bioremediation in the dissolved phase), IT Corporation developed a site plume model using the BIOPLUME II simulator to predict the behavior of the dissolved hydrocarbon plume, as influenced by passive bioremediation. This plume model accounted for contributions of fuel hydrocarbons to the dissolved phase by dissolution of the separate-phase source term over time. The results of the BIOPLUME II simulations suggested that the separate-phase source would disappear after approximately 20 years, with the dissolved plume persisting for an additional 20 years until passive bioremediation reduced concentrations below Maximum Contaminant Levels (MCLs).

In our opinion, the estimated 20-year dissolution period calculated in the original BIOPLUME II study cannot be substantiated because of problematic assumptions in the source diffusion model. Our calculations, using two alternative modeling approaches that take into account solubility limitations of hydrocarbon compounds in water, suggest much longer separate-phase source dissolution times, on the order of 50 to 100 years. However, we hypothesize that volatile losses of hydrocarbon components into the vadose zone, a process not considered in the initial site BIOPLUME II modeling, may represent a far more significant mechanism for source removal, potentially resulting in the depletion of the separate-phase source in approximately one-half the estimated dissolution time (i.e., a “best-case” estimate on the order of 30 years). Nevertheless, there is a high degree of uncertainty associated with this volatilization analysis because of the large number of poorly understood factors that influence transport of volatiles through the vadose zone (e.g., spatial variability in soil moisture content, lithology, transient nature of the separate-phase source, barometric pumping, etc.). As a result, the separate-phase source depletion estimates, combined with the BIOPLUME II dissolved phase bioremediation estimates, cannot produce a precise calculation for time to achieve cleanup. In our opinion, remediation of the dissolved hydrocarbon plume at GAFB is probably not likely to occur in a time frame of less than 50 years.

Calculations pertaining to dissolution and volatilization of the free product lens are presented in Appendix B.

3.2. Exposure Pathways

To pose a human health or ecological risk, the source of contaminants (e.g., residual free product) must be linked to receptors (e.g., water-supply wells) via pathways. Groundwater provides such a pathway through advective, dispersive, and diffusive transport of dissolved contaminants. However, passive bioremediation processes tend to limit the migration of dissolved hydrocarbons; the input of dissolved FHCs from residual secondary sources is balanced by FHC biodegradation integrated over the extent of the plume. This mass balance constraint is the likely explanation for the limited dissolved-phase plume lengths associated with majority of LUFT sites (Rice et al., 1995). Such a limitation of dissolved plume length restricts the likelihood that the groundwater pathway may be completed. Therefore, the evaluation of the groundwater exposure pathway is linked directly to an assessment of plume stability.

Several lines of field evidence at GAFB have been explored to assess the extent of passive bioremediation of the dissolved FHC plume in limiting plume movement. These include:

- Changes in concentrations of BTEX constituents over time and distance, supported by statistical analyses (i.e., Mann-Kendall test) (primary line of evidence).
- Changes in concentration ratios of BTEX components to those of presumed recalcitrant hydrocarbon tracers such as trimethyl- and tetramethylbenzene isomers (secondary line of evidence).
- Analyses of geochemical indicators of passive bioremediation (e.g., dissolved oxygen, nitrate, sulfate, manganese, iron, bicarbonate alkalinity, methane, pH, Eh) in selected monitoring wells (secondary line of evidence).

As stated in the Draft Natural Attenuation Monitoring Treatability Study Report, the results of the Mann-Kendall statistical analyses of BTEX concentrations are consistent with a stable FHC plume. However, while these results provide supporting evidence for passive bioremediation, they do not constitute conclusive proof of plume stability. Considerable scatter exists in the BTEX concentration data (based on four sampling events over a four-year period) and the spacing between monitoring wells used in the Mann-Kendall tests is a minimum of 300 ft (between MW-23 and MW-24), with a median value of 1450 ft. If the null hypothesis (i.e., the plume is not stable) is assumed for purpose of analysis, then, given the well spacing and mean flow velocities at the site, it is unclear if plume movement could be discerned during the time period involved, given the scatter in the data.

Analyses involving the ratios of BTEX concentrations to those of trimethyl- and tetramethylbenzene isomers, while again not inconsistent with passive bioremediation of BTEX compounds, also do not provide the strongest evidence supporting plume stability. This is because only two sets of monitoring wells, each consisting of two wells, were utilized in the analysis. This approach offers little opportunity to assess the potential for misinterpretation resulting from poor correlation of concentration ratios with distance.

Geochemical indicator data provide the strongest evidence for passive bioremediation of the dissolved FHC plume at GAFB. Data collected from site monitoring wells indicate a number of electron acceptors are being utilized in mineralization reactions involving dissolved FHCs. As discussed below and in Appendix C, simple geochemical reactive transport modeling can strengthen these observations by providing a framework for understanding integrated transport and biogeochemical processes in the subsurface.

In the absence of historical data which convincingly demonstrate plume stability or plume decline, the issue of plume movement can be addressed by probabilistic modeling. Using a conservative contaminant transport model (one that assumes a continuous source of contamination), probability distributions of the governing hydrogeological parameters (based on site data and best professional judgment), and the length of time the source has been active, the likelihood that plume has reached a steady-state condition may be evaluated in a quantitative manner. Such an analysis is described below and in Appendix C.

At LUFT sites, particularly those with significant quantities of free product present in the subsurface, the inhalation (vadose zone) pathway must be evaluated in addition to the ingestion (groundwater) pathway. At GAFB, vapor exposure pathways associated with the free product lens are unlikely to pose any substantial risks through inhalation, due partly to the large asphalt/concrete cap, and due partly to attenuation in the vadose zone. Risk calculations pertaining to the vapor exposure pathway are presented in Appendix D.

3.2.1. Groundwater Plume Stability Analysis

At the GAFB site, significant uncertainty exists concerning the length of time required for depletion of the free product source. Thus, a conservative model assuming constant source is warranted for forecasting plume behavior. Under such conditions, the plume concentration would be expected to stabilize in a steady-state condition when passive bioremediation processes are active. Geochemical indicator data demonstrate that passive bioremediation is indeed occurring at the site. Using a simple analytical solution to the advective-dispersive transport problem (Domenico, 1987), probabilistic modeling was conducted to forecast plume lengths based upon site-specific probability distributions of governing parameters (e.g., hydraulic conductivity, first-order hydrocarbon decay rate, length of time source has been active). Thus, in the absence of adequate historical monitoring data supporting plume stability, a simple model of expected plume behavior can be constructed to quantify likely plume lengths as a function of time. Forecast probable plume lengths can then be compared to observed plume lengths to assess the likelihood of further plume movement.

Forecasts of likely benzene plume lengths at GAFB, based on this modeling approach, generally match the observed plume length. Projection of plume behavior into the future (i.e., to the year 2022), under the assumption of a constant source (a conservative assumption) and constant hydrogeologic parameters, suggests that the probability that the plume will continue to advance over a significant distance is low (probably less than 10%). Thus, taking into account the length of time the contaminant source has been in existence, it is likely that the plume is approaching, or has already achieved, a steady-state condition. These conclusions are supported by mass balance considerations involving geochemical indicator species.

The calculations used in the modeling are presented in Appendix C.

3.2.2. Evaluation of Geochemical Indicators of Passive Bioremediation

Geochemical indicators of biodegradation provide evidence that is less dependent on the length of the monitoring period. Concentrations of natural attenuation geochemical indicator species (e.g., dissolved oxygen, nitrate, sulfate, iron, methane, redox potential) have been collected from 16 monitoring wells at GAFB as part of a natural attenuation monitoring study. Observed variations in hydrocarbon concentrations and key geochemical indicators of biodegradation across the site have been evaluated using a reactive transport model screening tool coupled with the analytical solute transport model of Domenico (1987). The purpose of the modeling was to verify, in a semi-quantitative manner, that the observed variations in site geochemistry are indeed consistent with those expected as a result of biodegradation processes.

The modeling analyses is explained in Appendix C. The results indicate that biodegradation reactions fully explain the observed changes in groundwater geochemistry, supporting the hypothesis that passive biodegradation processes are actively remediating the hydrocarbon plume.

3.3. Receptors

3.3.1. Present and Anticipated Future Human Health Receptors

Population centers are clustered south of GAFB. Population counts within five miles of the plume center, including 6,815 individuals that were part of the GAFB census tract, are shown on

Table 1. It is assumed that this particular population will diminish as GAFB is closed, but the general population in the area may increase based on transformation of GAFB to the Southern California International Airport (SCIA). Currently this is only in the planning stages. The majority of the population is located south of GAFB; to the north-east a population of 1,169 individuals are spread out over a large area. These individuals are likely to use private well water.

Table 1. Population distribution around GAFB.

Radius from FHC plume center (miles)	Population
1	6,815
2	7,829
3	12,890
4	15,129
5	20,855

Population in Victorville has experienced an approximate nine percent/year exponential increase since 1980. This growth has decreased substantially, and was no more than 3.5 percent/year over the last year. Growth is greatest around the city itself, and becomes less to the north. A moderate six percent growth rate will increase water usage approximately 4.5 times. The Department of Water Resources expects an overall increase of urban growth demand of three percent/year, which may be inappropriately low considering the recent growth of the Victorville and Antelope Valley areas and the possible conversion of GAFB into a regional airport. Groundwater overdraft for the entire South Lahontan Region is approximately 70,000 acre-ft/year, which is expected to remain constant due to a reduction in agricultural usage and importing water from the California Water System.

Victor-Valley Water (VVW) expects to supply the SCIA with water from a groundwater source that will be piped in from the Victorville area (Don Songer, Personal Communication, 1996). VVW currently does not plan to use the groundwater on the GAFB site itself. The California Department of Health Services database shows supply wells within a two-mile radius of GAFB, supplying the population to the south of the base and the City of Adalento. The Department of Water Resources (DWR) database states that the production capacities of these wells range from 100 to 1,200 gallons per minute (gpm), and are screened in the Regional (lower) aquifer at depths ranging from 500 to 610 ft below ground surface. These wells are all upgradient of the base, and would not be affected by any impacted groundwater at GAFB. Downgradient of the OU-2 site, Victor Valley, Waste Water Reclamation Authority, uses two wells screened in the upper aquifer, which have pumping capacities of 500 gpm. These wells are used for non-potable industrial applications only (JMMCE, 1988).

Two miles north east, there are about 50 to 60 private wells, situated mostly along Highway 66 (Jeff Ricciardi, personal communication, 1996). These wells draw their water directly from the Mojave River alluvial bed. There are a few wells between GAFB and the Mojave River bed area, but the zone of influence for these small wells will not affect the GAFB OU-2 FHC plume. There are no private water-supply wells within one-half mile of the release.

The potential for human receptors to ingest groundwater impacted by the FHC plume is negligible, considering current population patterns, proposed water plans for the area, and the apparent stability of the GAFB hydrocarbon plume. Buildings in the immediate vicinity of the plume are theoretical receptors with regard to hydrocarbon vapors. However, the risk of exposure is negligible as the pathway is not complete (Appendix C).

3.3.2. Ecological Risk Receptors

No ecological risk receptors have been identified.

4. Summary and Recommendations

For a dissolved hydrocarbon plume to pose a risk to human health or the environment, a source, pathway, and receptor must all simultaneously co-exist. The absence of any one of the three implies that there is no associated risk. At GAFB, each of these components has been evaluated independently:

Sources. An estimated 350,000 gal of free product remain in the subsurface. It is unlikely that current free product removal efforts will be able to remove the majority of the contaminants. Natural dissipation processes, including dissolution and volatilization, will probably require at least 30 years to remove a majority of the volatile, soluble components (BTEX).

Pathways. In our judgment, historical groundwater monitoring and recalcitrant tracer analyses at GAFB are not by themselves sufficient to provide convincing evidence of plume stability or decline. Nevertheless, geochemical indicator data do provide secondary evidence strongly supporting the action of passive bioremediation. Contaminant transport modeling suggests a high probability that the dissolved plume has at least achieved a steady-state condition. A significant vapor exposure pathway through the vadose zone is unlikely.

Receptors. Accounting for current and projected future local population and land use issues, it appears that there are no receptors (water supply wells, ecological risk receptors) at risk of detrimental impact by the dissolved FHC plume in groundwater.

According to the sources-pathways-receptors conceptualization, the FHC contamination in the subsurface at GAFB does not present a risk to human health or the environment. Receptors cannot be identified and passive bioremediation is likely to have stabilized the dissolved plume in groundwater, restricting the ingestion pathway. In terms of risk to potential existing receptors, the presence of the residual source (i.e., free product lens), and its rate of removal, are therefore not important risk-management concerns.

The need to meet beneficial use cleanup objectives must be considered as part of any risk-management strategy at GAFB. When considering beneficial use impacts, groundwater itself becomes defined as a receptor. As such, plume stability is replaced by time-to-cleanup as the key technical issue. In the case of GAFB, it is difficult to base a risk-management decision on time to restore beneficial use because the time needed to completely remediate groundwater to below MCLs, with or without the assistance of engineered free product removal, cannot be estimated with meaningful certainty.

The likely long-term persistence of long-chain, high molecular weight residual hydrocarbons, which are highly insoluble, non-volatile, and somewhat resistant to biodegradation, further complicates the issue. These long-chain FHC components can only be partly removed by very expensive remediation technologies such as steam injection and recovery.

It is important to note that the volume of affected groundwater[3] is relatively small and is largely confined to the area below the extensive concrete landing and operations area of the proposed SCIA. This quantity of affected water has been estimated to constitute approximately 2,000 acre feet (IT, 1992). This volume of potentially impacted groundwater where beneficial

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[3] As defined as the volume of water encased by the MCL (i.e., 5 ppb) contour for benzene.

use is denied can be expected to remain fixed in space and not to expand further. However, several safeguards do exist to protect potential future risk receptors who may attempt to utilize groundwater at the site:

- Because the hydrocarbon plume remains on Air Force property, institutional controls can be implemented to assure against hydrocarbon exposure risks associated with unanticipated land use or groundwater use activities.
- Future anticipated land use (i.e., development of a commercial airport) largely precludes the use of underlying groundwater for drinking water purposes, at least for the foreseeable future.
- In the unlikely future event that institutional controls are not present, taste and odor thresholds are a potent indicator of hazard. When there is awareness, hazards are typically avoided, thus, removing the potential impact of the hazard and removing the risk. A strong indicator of hazard is the low taste and odor thresholds associated with FHC products. At levels where there would exist a large cancer risk (e.g., 10^{-4} cancer risk), the associated odors and tastes would cause a voluntary avoidance of that water for drinking and showering, although workers may not show the same avoidance for inhalation of fugitive vapors. Due to this, ingestion or inhalation of water from showering are improbable and the risk associated with direct ingestion or showering with these waters is minimal.
- Natural source dissipation and passive bioremediation will eventually remediate the site below MCLs.

4.1. Specific Recommendations

Engineered Source Removal. At GAFB, free product removal efforts are not necessary to reduce an existing exposure hazard at the site. Operation of free product recovery systems may have little impact on the time to allow permissible beneficial use of groundwater affected by OU-2 FHCs, and the contribution of free product removal operations to reducing cleanup time cannot be reliably estimated.

Further, residual long-chain FHC components in the area of the original FHC plume will be present for greater than 50 years and will limit the beneficial use of the groundwater in this area. The technical impracticality of complete removal of free product and long-chain FHC components trapped in the subsurface at GAFB limit cost/benefit trade-offs of actively engineered source removal operations, i.e., there may be little benefit realized for the cost incurred. The principal benefit of continued operation of actively engineered free product removal processes may be to demonstrate good faith and to gain acceptance for a passive bioremediation remedial alternative. At a minimum, free product recovery operations should not be continued once recovery begins to decline.

Monitoring and Closure. Groundwater monitoring should continue on an annual basis for at least two monitoring wells at the downgradient margin of the plume for at least five more years to provide additional supporting evidence for plume stability. Once stability has been demonstrated, the OU-2 FHC release site can be safely closed.

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Appendix A

George Air Force Base Site Assessment Evaluation Letter

Lawrence Livermore National Laboratory

July 30, 1996

Bob Sommer
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13436 Sabre St.
Victorville, CA 92394-5000

Dear Bob:

The Lawrence Livermore National Laboratory Expert Committee has reviewed the methods and findings of the site investigations conducted at George Air Force Base (GAFB), located in Victorville, California, with regard to subsurface releases of aviation fuel. These site investigations have been conducted by IT Corporation and others. Included is our evaluation of the adequacy of the site conceptual model and risk characterization as a credible basis for applying risk-based corrective action (RBCA), emphasizing natural attenuation as a means of remediation, to achieve site closure.

This letter represents the first of two deliverable documents as part of our overall assessment. It is intended solely as a brief review of the existing site data and risk characterization models; recommendations regarding additional data needed to complete the site model review are provided. Specifically, the review included:

- An assessment of site characterization and the contaminant distribution model, based upon conformance with standard environmental investigation practices and sound scientific judgment;
- A preliminary assessment of bioattenuation signatures, based upon presentation of multiple lines of evidence such as natural geochemical indicators and changes in plume composition over time;
- An assessment of risk characterization, based upon our judgment as to how significant uncertainties in risks posed to potential receptors have been characterized.

Detailed analyses of key assumptions and an assessment of site-specific natural attenuation will be provided in a follow-on report as a separate deliverable item. With regard to GAFB, the dissolution rate of the free product lens and the capacity for natural attenuation processes to prevent further downgradient migration of the dissolved hydrocarbon plume will be the subject of focused study.

Site Conceptual Model

In our opinion, the distribution of contaminants at GAFB has been reasonably well characterized. Petroleum hydrocarbons (originally JP-4 aviation fuel) are present in the subsurface environment at GAFB as a result of leaks from underground tanks and piping systems. A significant volume of separate phase product, estimated to be on the order of 350,000 gallons, persists on top of the water table, covering an area of approximately 32 acres, with product thicknesses ranging from a thin sheen to several feet. A plume of dissolved fuel hydrocarbon compounds (FHCs) exists in the underlying groundwater, extending a few hundred feet downgradient of the free product lens. Isolated pockets of low concentrations of dissolved halogenated hydrocarbons (TCE, PCE, 1,1-DCA) have also been noted in site groundwater.

The site hydrogeologic model is well developed (37 monitoring wells have been installed onsite). The site is underlain by alluvial sediments consisting of unconsolidated sands, silts, clays, and gravels in an arid climatic setting. An unconfined water-bearing zone underlies the site (depth to the water surface is on the order of 100 feet); this water-bearing zone is in turn underlain by a clay aquiclude and a regional aquifer. Hydraulic conductivity values have been calculated from a number of pumping tests and aquifer tests (although analyses associated with the two methods have produced estimated values which are not entirely self-consistent). Taken with interpolated hydraulic head values and porosity estimates, these data suggest groundwater movement in a north-northeasterly direction at a rate of tens to hundreds of feet per year. Little recharge/evapotranspiration is expected in association with the unconfined aquifer.

The spatial extent of the dissolved FHC constituents/BTEX in groundwater appears to reasonably well-characterized over individual sampling rounds, although long-term historical trends in individual wells are not available. Concentrations of natural attenuation geochemical indicator species (e.g. dissolved oxygen, nitrate, sulfate, iron, methane, redox potential) have also been collected from 16 monitoring wells as part of a natural attenuation monitoring study. Clear evidence has been presented indicating natural bioattenuation processes are occurring at GAFB. These include apparent shrinkage of BTEX constituent plumes with time, loss of BTEX components in comparison to recalcitrant dissolved FHC constituents (trimethylbenzene isomers), and changes in geochemical indicator species which vary in space in a manner consistent with expected bioattenuation redox regimes.

Site Risk Characterization and Management Strategies

Standard risk assessment analyses were conducted for the GAFB site. Because of the depth at which the contamination occurs, the present land use at GAFB, and the presumed large distances to potential human and ecological risk receptors downgradient, risks to human health through common exposure pathways and to the environment appear to be low. However, we have not been able to identify locations and screened intervals of existing water supply wells downgradient of the GAFB site in the site documentation. Such information needs to be provided if available to apply risk based corrective action to the site.

Current remediation techniques applied at GAFB include free product removal, capillary fringe bioventing, and natural attenuation of dissolved FHCs in groundwater. Free product remediation consists of mobile and permanent free product recovery systems, which remove approximately 160 gallons of free product per day, with a cumulative total of approximately 32,000 gallons to date. The bioventing program has to date consisted largely of a treatability test. Natural attenuation is expected to provide the means for controlling and eventually remediating the dissolved FHC plume. In addition to presenting parallel lines of evidence supporting the occurrence of bioattenuation at GAFB, modeling studies using BIOPLUME II were conducted by IT to quantify the expected decline of the hydrocarbon plume over time as a result of natural attenuation. Sensitivity studies were conducted to evaluate the significance of parameters such as dispersivity and anaerobic decay rate on estimated time to achieve cleanup (i.e. time required to reach MCLs). The conclusion of these modeling exercises was that cleanup of the dissolved FHC plume would be achievable within 40 years.

In principle, the application the BIOPLUME II model for evaluating the future behavior of the dissolved FHC plume at GAFB is reasonable, provided that (1) uncertainties in model parameters and contaminant sources are addressed, and (2) the model is not relied upon as the exclusive means for assessing future contaminant behavior. The source term in the GAFB BIOPLUME II model is based upon quantifying Fickian diffusive solute fluxes across the free product-water interface. These calculations are very sensitive to assumptions regarding the mass of the free product, boundary concentrations, concentration gradient, and so forth. Our preliminary evaluation of the free product dissolution problem, using a model based on a dissolution mixing zone factoring in regional groundwater flow, suggests that the predicted cleanup time projected by the BIOPLUME model is subject to considerable uncertainty. In our opinion, this uncertainty must be addressed by additional analyses, as the estimated time that natural attenuation can be expected to remediate the site depends on the quantity of free product present and the rate of mass removal. In response, more detailed analyses of free product dissolution, using alternative models (e.g. time-dependent diffusion, mixing zone) will be undertaken by the Expert Committee for inclusion in the follow-on report.

Clarification of several issues concerning the free product lens will aid in our analyses. Experience suggests that free product removal efforts generally do not succeed in removing more than about 30% of the spill volume. Based on current free product estimates, the current mass removed represents approximately 10% of the estimated free product source mass. Historical free product removal rates may help bound the uncertainty in the source mass. Also, we note that the estimates of free product mass present in the subsurface at GAFB have tended to increase through time, ranging from roughly 250,000 gallons to well over 400,000 gallons. We recognize that this may be a result of further characterization as the investigation has progressed. However, it would be helpful if we were provided with the explanation for the range of values reported would also be provided so that we may better understand the variability of the free product mass. Finally, compositional variations in the weathered free product, in comparison to unweathered JP-4, may provide insights into the rate of volatilization of lighter-weight (and therefore more soluble) components.

In addition to addressing the source term uncertainty, the potential for natural attenuation mechanisms to limit the extent of the dissolved FHC plume will also be evaluated by the Expert Committee as part of the follow-on site report. This evaluation will consist of applying alternative plume bioattenuation models to the GAFB groundwater data set, taking into account geochemical bioattenuation indicators. The results of these analyses will be used in an attempt to validate the natural attenuation conceptual model.

Summary

Subsurface investigations conducted at GAFB by IT Corporation appear to be satisfactory in terms of characterizing the nature of the subsurface environment and the distribution of contaminants. Thus, we do not foresee any need to collect additional field data for the application of the RBCA decision-making process. The natural attenuation study has provided credible evidence that dissolved FHCs in groundwater underlying the site are indeed undergoing bioattenuation to some extent. Furthermore, it appears that existing site data may be used to construct arguments that the dissolved FHC plume will at least remain stable for the foreseeable future (i.e. the plume in all likelihood will not advance further in the downgradient direction). This scenario will be investigated by the Expert Committee using additional plume analyses, including a quantitative assessment of bioattenuation signatures.

In our opinion, the cleanup time estimates provided by modeling analyses using BIOPLUME II are characterized by significant uncertainty. This is primarily because of potential uncertainties with regard to the source term associated with the large free product volume. As a result, given the existing data, it is difficult to ascertain the length of time shallow groundwater immediately underlying the site will continue to be impacted by petroleum hydrocarbons. The Expert Committee will address the uncertainty associated with the time required for free product dissolution by additional quantitative analyses in the follow-on site report. To assist in this effort, the following data are requested:

(1) Historical free product recovery estimates;
(2) A brief summary explanation of the uncertainty in free product mass estimates;

(3) Chromatographs from any historical free product analysis to evaluate product weathering.

Also, to facilitate risk analyses as part of the RBCA decision-making process, we request:

(4) Downgradient water supply well locations and screened intervals (if available).

We look forward to preparing the GAFB site report following receipt of this information.

Sincerely,

David W. Rice
Project Director

Walt W. McNab, Jr.
Expert Committee Lead for George A.F.B.

cc: John Adams, SWRCB
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Appendix B

Free Product Dissolution/ Volatilization Analysis

Appendix B

Free Product Dissolution/Volatilization Analysis

B-1. Background

The source term used to describe the contribution of BTEX components from dissolution of the non-aqueous phase liquid (NAPL) pool in the BIOPLUME II model involved the calculation of steady-state diffusive fluxes based on Fick's law and then emulating the fluxes with a series of injection wells operating at very low flow rates. Using an assumed concentration gradient across the NAPL-groundwater interface, diffusive fluxes were assumed to persist at constant levels until BTEX components were depleted. The assumption of steady-state influxes of BTEX components into the dissolved phase is only a crude approximation because concentration gradients, and hence solute fluxes, across the interface will tend to decrease over time, but persisting for a longer period than predicted by a steady-state model. Nevertheless, the assumption of a steady-state flux provides a reasonable order-of-magnitude approach at quantifying the problem. However, the specific approach used in the BIOPLUME II model to simulate diffusive fluxes of BTEX across the NAPL-groundwater boundary is problematic for two principle reasons:

1. The definition of concentration gradient is arbitrary. Fluxes are calculated based upon a concentration gradient defined over a distance of 20 ft between the concentrations of BTEX components in the JP-4 NAPL phase and the highest concentrations of BTEX measured in groundwater monitoring wells.
2. Limited solubility of BTEX components in the aqueous phase is not considered. This is a key omission; pure-phase BTEX components are characterized by solubilities in water that are less than concentrations in JP-4 NAPL (e.g., 3,880 mg/L benzene concentration in NAPL—based on a weight fraction of 0.5 percent—versus a pure-phase solubility of 1,770 mg/L). In addition, because JP-4 NAPL is a mixture of a large number of components, solubilities of individual species such as benzene will be less than those of their pure-phase equivalents as approximated by Raoult's law[1], ignoring cosolvency effects (see discussion below). As a result, concentration gradients calculated using BTEX concentrations in the NAPL phase are not physically meaningful.

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[1] Raoult's law states that the partial pressure of a given species in the gas phase is equal to the mole fraction of the component in the liquid phase multiplied by the partial pressure of the pure phase substance. By analogy, the aqueous solubility of a component in a NAPL mixture (e.g., benzene) is equal to its mole fraction in the liquid phase multiplied by the aqueous solubility of the pure substance. This idealization does ignore cosolvency effects, which tend to raise the solubility of a component above that predicted by Raoult's law. However, in the case of JP-4, it is likely that benzene and the other BTEX components are not subject to strong cosolvency effects, given that highly soluble additives such as methanol or methyl tertiary butyl ether (MTBE) are not present in the mixture.

B-2. Plume Dissolution Model

A more rigorous approach is to recognize that 1) aqueous phase solubilities of individual components in the NAPL mixture control diffusive transport across the NAPL-water interface, and 2) concentration gradients across the NAPL-water interface are influenced by the lateral advective transport of dissolved hydrocarbons from dissolution of any NAPL present in the upgradient direction. Hunt et al. (1988) presented a steady-state conceptual model of the dissolution of a NAPL pool as described by the equation,

$$v\frac{\partial c}{\partial x} = D_z \frac{\partial^2 c}{\partial z^2} \tag{B-1}$$

subject to the boundary conditions,

$c(0 < x \leq L, z = 0) = c_s$
$c(x, z = \infty) = 0$
$c(x = 0, z) = 0$

where v refers to the groundwater pore velocity, $\partial c/\partial x$ the concentration gradient in the horizontal direction, D_z the effective dispersion coefficient in the vertical direction, and $\partial^2 c/\partial z^2$ the gradient of the concentration gradient in the vertical direction. Equation B-1 states that the downward dispersive vertical movement of the dissolved contaminant at any point below the NAPL-water interface is equal to the lateral advective flux. The solution to this equation is:

$$c(L,z) = C_s\, erfc\left[\frac{z}{2\left(\frac{D_z L}{v}\right)^{1/2}}\right] \tag{B-2}$$

where L refers to the distance along the NAPL product pool from the upgradient end, z the vertical depth below the NAPL-water interface, and C_s the effective aqueous solubility of the NAPL component. Equation B-2 may be used to evaluate solute fluxes across the NAPL-water interface by numerically differentiating concentration with distance to obtain a concentration gradient estimate at point L along the base of the NAPL plume:

$$\frac{\partial c}{\partial z}_{z=0} = \frac{c(L,\delta z) - c(L,0)}{\delta z} \tag{B-3}$$

where δz is some small distance (e.g., 1×10^{-5} m), and then multiplying by the effective dispersion coefficient:

$$\frac{mass}{time} = -D_z \frac{\partial c}{\partial z}_{z=0} A \tag{B-4}$$

where *A* refers to a horizontal cross-sectional area. Dissolution time can then be calculated by assuming a mean thickness for the NAPL pool and hence the benzene mass per unit horizontal cross-sectional area.

Table B-1. Parameters for dissolution model of Hunt et al. (1988).

Parameter	Value	Notes
Benzene mole fraction in JP-4	Lognormal. Mean = 0.56%; standard deviation = 0.28%.	Pure benzene solubility = 1770 mg/L; Raoult's law approximation; mole fraction of benzene assumed equal to its weight fraction in JP-4, 0.5% (IT, 1996). Variations in JP-4 composition and departures from the ideality of Raoult's law may explain slightly higher concentrations of benzene noted in some GAFB groundwater samples.
D_z (effective vertical dispersion coefficient)	Lognormal. Mean = 4.4×10^{-9} m^2/sec; standard deviation = 8.91×10^{-9} m^2/sec. Corresponds to the 1st-percentile = 10^{-10} m^2/sec and the 90th percentile = 10^{-8} m^2/sec.	Based on vertical mixing model and Peclet number considerations. See discussion in text.
K, hydraulic conductivity	Lognormal. Mean = 61.2 ft/day; standard deviation = 30.4 ft/day. Corresponds to the 10th-percentile = 30 ft/day and the 90th-percentile = 100 ft/day.	Based upon site data (IT, 1996).
∇h, hydraulic gradient	Lognormal. 25th-percentile = 0.002; 75th-percentile = 0.003.	Based upon site data (IT, 1996).
ϕ, porosity	Normal. Mean = 0.25; standard deviation = 0.03.	Postulated.
A (area of NAPL pool)	Normal distribution. Mean = 1,860,000 ft^2; standard deviation = 186,000 ft^2 (assumed to be equal to 10% of the mean for simplicity).	IT (1996).
V (volume of NAPL pool)	Normal distribution. Mean =350,000 gal; standard deviation = 35,000 gal (assumed to be equal to 10% of the mean for simplicity).	IT (1996).

A Monte Carlo simulation was conducted using Equations B-2 through B-4 to provide insight into the amount of time required for benzene to dissolve out of the free product pool at GAFB by assuming the system remains at steady-state. Probability distributions for the governing parameter are shown on Table B-1; values were estimated from site documentation (e.g., IT, 1992) or otherwise estimated based on judgment of likely site conditions. Modeling consisted of programming Equations B-2 through B-4 into a Microsoft Excel spreadsheet and then using the Crystal Ball add-in package (Decisioneering, Inc., 1996) for Excel to run a total of 10,000 realizations with the prescribed parameter distributions.

Effective solubility of benzene, C_s, was calculated based on the pure phase solubility of benzene, C_p, (1,770 mg/L) and a Raoult's law approximation using the mole fraction of benzene in JP-4, X_b,

$$C_s = C_p X_b \tag{B-5}$$

Groundwater velocity was calculated using Darcy's law,

$$v = \frac{K \nabla h}{\phi} \tag{B-6}$$

where K is the hydraulic conductivity, ∇h the hydraulic conductivity, and ϕ the porosity. Assuming a circular NAPL pool as a simplifying assumption, a representative distance along the base of the pool representing an average dissolution rate can be assumed to equal the radius of the pool, thus the parameter L in Equation (B-2) was estimated by:

$$L = \sqrt{\frac{A}{\pi}} \tag{B-7}$$

where A is the area of the NAPL pool in plan view.

Cleanup times were forecast by dividing the benzene mass per unit area in the NAPL pool by the modeled flux rate (as calculated by Equation B-4). Benzene mass per unit area was estimated by first dividing the NAPL volume by its area to yield the NAPL pool mean thickness, then assuming a density of 0.8 g/cm^3 to convert to mass per unit area, and finally correcting this value by the benzene mole fraction (assumed equivalent to the mass fraction). The cumulative distribution function resulting from the Monte Carlo analyses for total dissolution time of benzene out of the NAPL phase is shown on Figure B-1. The median value is on the order of 50 years. Because of the steady-state assumption, the estimates produced are conservative because benzene concentrations in the NAPL, and hence along the saturation boundary layer, in reality would decline with time. This would result in a decrease in gradient and hence a reduction in the dissolution rate.

B-2.1. Effective Vertical Dispersion Coefficient

Vertical fluxes calculated by the methodology outlined above show a high degree of sensitivity[2] to the vertical dispersion coefficient, D_z, shown in Equation B-1. In principle, this value could

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[2] Sensitivity analysis of the Monte Carlo simulation output, based on contribution to variance in rank correlation, suggests that the effective vertical dispersion coefficient has the most significant effect by far on cleanup time estimates (approximately 85% of the variance is attributable to uncertainty in D_z), followed by hydraulic conductivity (11%), NAPL volume (1.5%), hydraulic gradient (1%), and NAPL area (1%).

range from the effective molecular diffusion coefficient, on the order of 1×10^{-10} m^2/sec, to several orders-of-magnitude higher if vertical hydrodynamic dispersion is a significant process at the NAPL-water interface. One method for evaluating a realistic range of possible vertical dispersion coefficients is to examine the predicted concentrations in the underlying aqueous phase as a function of depth according to Equation B-2. Because groundwater samples are not usually collected at discrete points but rather are a reflection of integrated measurements over the length of a well screen, it is appropriate to consider depth-averaged concentrations which could be measured under the steady-state assumptions used in the development of Equation B-2.

Calculated vertically-averaged concentrations of benzene (at plume center) along discrete depth intervals as a function of the vertical dispersion coefficient are shown on Table B-2 (assuming C_s = 8.85 mg/L, K = 60 ft/day, ∇h = 0.002, ϕ = 0.25, and L = 230 m). Given historical measurements of benzene concentrations in groundwater at GAFB provided in site documentation, it appears that values of D_z greater than 1×10^{-7} m^2/sec produce vertically-averaged concentrations of benzene that exceed observation to a considerable degree, especially when averaged over a depth of 10 m.

Table B-2. Vertically-averaged concentrations parts per billion (ppb) versus effective vertical dispersion coefficient.

Depth (m)	1×10^{-10} m^2/sec	1×10^{-9} m^2/sec	1×10^{-8} m^2/sec	1×10^{-7} m^2/sec
0	8,850	8,850	8,850	8,850
0.1	6,850	8,183	8,638	8,783
0.5	2,755	5,769	7,799	8,515
1	1,503	3,719	6,796	8,181
2	787	1,986	5,072	7,525
5	324	818	2,390	5,731
10	164	413	1,208	3,028

A second approach at quantifying D_z is to consider the nature of the mixing regime. This is accomplished through evaluating the dimensionless Peclet number, which is defined as average pore velocity multiplied by average throat velocity divided by the effective molecular diffusion coefficient. The effective molecular diffusion coefficient is defined as molecular diffusion coefficient divided by a tortuosity factor. The Peclet number is a measure of the contribution to mixing of mechanical mixing compared to molecular diffusion. At values much less than 1.0, molecular diffusion acts as the dominant mixing mechanism and mechanical dispersion may be neglected. At values much greater than 1.0 the opposite is true. When the Peclet number is in the range of 0.5 to 5 it must be assumed that both molecular diffusion and mechanical dispersion are significant and must be accounted for. Various Peclet numbers for a range of throat diameters are listed on Table B-3 and B-4 using site specific parameters for the GAFB site and the properties of benzene.

Table B-3. Peclet number parameters.

Molecular diffusion coefficient (m^2/s)	8.3×10^{-10} m^2/sec
Tortuosity	2
Porosity	0.2
Effective diffusion coefficient (cm^2)	8.3×10^{-11} m^2/sec
Average velocity (cm/s)	2.5×10^{-7} m/sec

Table B-4. Peclet number versus pore diameter.

Pore diameter (m)	Peclet No.
1×10^{-3}	3.0
1×10^{-4}	0.3
1×10^{-5}	0.03

These results indicate that mixing is probably dominated by molecular diffusion. In the unlikely case that the throat diameter is as large as 1.0 millimeter, the Peclet number ranges into the region where mechanical mixing should be considered along with diffusion. However, at more realistic throat diameters of 1/10 to 1/100 of a millimeter, mixing is completely dominated by molecular diffusion and mechanical mixing can be neglected. Thus, taken with dissolved BTEX concentrations measured in groundwater near the NAPL plume, these analyses suggest that the vertical dispersion coefficient is generally small. For modeling purposes, therefore, a lognormal distribution of the effective vertical dispersion coefficient between 1×10^{-8} and 1×10^{-10} m^2/sec was assumed.

B-2.2. An Alternative Dissolution Model Based Upon a Mixing Zone Assumption

As an alternative means for estimating NAPL dissolution time, a second modeling approach, based on a mixing zone concept for the NAPL-groundwater interface, was also evaluated. This approach simply assumes that a finite thickness mixing zone exists in groundwater immediately below the NAPL pool, which is saturated with benzene[3]. In this case, dissolved contaminants are flushed away from the NAPL pool at a rate equal to the concentration, times the advective pore velocity, times the cross-sectional area of the mixing zone underneath the plume. A Monte Carlo analyses was performed using the same constraints as the first model for gradient, porosity, hydraulic conductivity, and NAPL pool volume and area. Two probability distribution models were used to described the thickness of the mixing zone. The first model (Case 1) assumed an

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[3] Both models are insensitive to the weight fraction/mole fraction of benzene, assuming a Raoult's law relationship. For example, if the weight fraction of benzene in JP-4 were 2% instead of 0.5%, its solubility, according to Raoult’s law, would be 35.4 mg/L, so the flux out the NAPL phase would be four times as high. At the same time, however, there would be four times as much benzene to remove, so the effects of higher benzene concentrations would tend to cancel one another.

exponential distribution of mixing zone thickness, with a rate coefficient of 2.0. The second model (Case 2) assumed a uniform probability distribution for the mixing zone thickness, ranging from 0.01 m to 1.0 m. The results of both of these simple models, illustrated on Figure B-1, also suggest a long dissolution time, generally much greater than 100 years.

As expected, sensitivity analyses reveal that the uncertainty regarding the depth of the mixing zone is the primary factor in influencing variance in cleanup time estimates (84% and 69% of the contribution to variance for Case 1 and Case 2, respectively) followed by much smaller contributions due to uncertainties in hydraulic conductivity, gradient, and NAPL pool volume.

B-2.3. Volatile Losses Into the Vadose Zone

In environments not characterized by large recharge, the transport of chemicals in the vadose zone is mainly a diffusive process. Mayer et al. (1974), employing a methodology by which water transport was assumed to be negligible, proposed five different models for pesticide movement due to diffusive forces alone. The methodology used a separation of variables approach as discussed by Carslaw and Jaeger (1959) and has been used by others as a screening level tool (Jury et al., 1983, 1984a,b,c, and 1990). A similar approach using boundary conditions appropriate for the site is discussed below.

Vapor phase transport of benzene from the NAPL plume was examined to determine the time frame in which it would be removed. The equation of diffusive transport, written in terms of the total concentration is:

$$\frac{\partial C_T}{\partial t} = D_{eff} \frac{\partial^2 C_T}{\partial z^2} \tag{B-8}$$

with the total concentration being:

$$C_T = C_g \left(\theta_g + \frac{\theta_l}{H} + \frac{\rho_b K_d}{H} \right) \tag{B-9}$$

θ_l is the volumetric water content[4], θ_g is the vapor content, H is the dimensionless Henry’s law constant, ρ_b is the bulk soil density, and K_d is the distribution coefficient for the chemical (based on a reported value by IT Corp., 1996).

The effective diffusion coefficient is based on the gas diffusion coefficient (the water diffusion coefficient has been neglected), and is:

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[4] Sediments in the vadose zone environment at GAFB consist of silt and sand, with an average effective porosity of 0.18. The stated volumetric water content provided in the GAFB Operable Unit 2 Natural Attenuation Program (LLNL Expert Committee), May 1996 report is a misnomer (Larry Tyner, Personal communication, IT Corp., 1996). The volumetric water content is given as an average 0.158, distributed from 0.15 to 0.23. Based on the given ranges of porosity, this would correlate to a very moist vadose zone environment, in an area characterized by low rainfall rates and a large concrete cap covering most of the site. It is therefore assumed that specified water content is actually the saturated fraction, resulting in a range of volumetric water content from 0.023 to 0.078. Questions remain as to the methodology of the tests performed to determine saturated fraction and porosity.

$$D_{eff} = \frac{D_g}{R\tau} \tag{B-10}$$

The unsaturated retardation factor, *R*, is defined by:

$$R = 1 + \frac{\theta_l}{H\theta_g} + \frac{\rho_b K_d}{H\theta_g} \tag{B-11}$$

and the tortuosity, τ, for gaseous diffusion in air-filled pore spaces only, is the Millington (1959) equation corrected by Falta et al. (1992),

$$\tau = \frac{\phi^2}{\theta_g^{7/3}} \tag{B-12}$$

The boundary conditions for the problem is one of assumed zero flux across the low-permeability concrete cap, with a constant concentration at the NAPL-vadose zone interface. The NAPL dimensional area is large enough in comparison to the vadose zone thickness that a one-dimensional (1-D) idealization is for estimating a time scale necessary to reach steady state in the vadose zone. The boundary conditions are shown in the conceptual scenario (Fig. B-2),

$$\begin{array}{lll} t = 0 & C_{To} = 0 & 0 \le z \le L \\ x = 0 & C_{Ti} = C_i & \\ x = L & \dfrac{\partial C_T}{\partial z} = 0 & \end{array}$$

Using a separation of variables approach, it may be shown that

$$\frac{C}{C_{Ti}} = 1 - \sum_{n=0}^{\infty} \frac{2(-1)^n}{(n+0.5)n} \exp\left[-(n+0.5)^2 \pi^2 \frac{t}{L^2/D_{eff}}\right] \cos\left[(n+0.5)\pi \frac{L-Z}{L}\right] \tag{B-13}$$

The result of this series is shown in Figure B-3. This equation has been nondimensionalized in space, so that the figure is representative of any concentration at $x = 0$. For this problem, the initial concentration within the vadose zone is taken to be zero. For a volumetric water content of 0.028, after approximately 70 years, the concentration is within 95% of the steady-state condition possible within the vadose zone above the plume. The equivalent steady state is 315 years for a water content of 0.078. These steady state conditions give a gas phase concentration for benzene of approximately 2.5 parts per million (ppm).

The vapor phase concentration of 2.5 ppm, which is the driving force, is derived from an assumption of a constant surface concentration at the NAPL surface. Although this is recognized to be conservative, this estimation is primarily performed to develop an “order of magnitude” model of the relative contributions of dissolution vs. volatilization.

The total contaminant mass that the vadose zone has the capacity to assimilate is derived from the total concentration times the volume. It is found in the above conservative estimate that the vadose zone, idealized as a one-dimensional slab, has the capacity to absorb approximately 1.4 times the benzene assumed to be resident within the NAPL. Using this constant driver concentration, the vadose zone is capable of absorbing the full amount of benzene in 25 years for the water content of 0.028, and 100 years for the water content of 0.078.

This analysis does not take account into several factors, including constituents already within the vadose zone, radial transport outward at the fringes, variable water content, or possible degradation. Due to the relatively impermeable boundary condition at the surface, and therefore a low diffusive flux of oxygen, degradation may be oxygen limited near the center of the plume, varying outwards towards the edges. There are 10 biovents that are installed around the site above the plume that are providing oxygen, but without design details of these biovents, the oxygen content within the vadose zone is currently unknown.

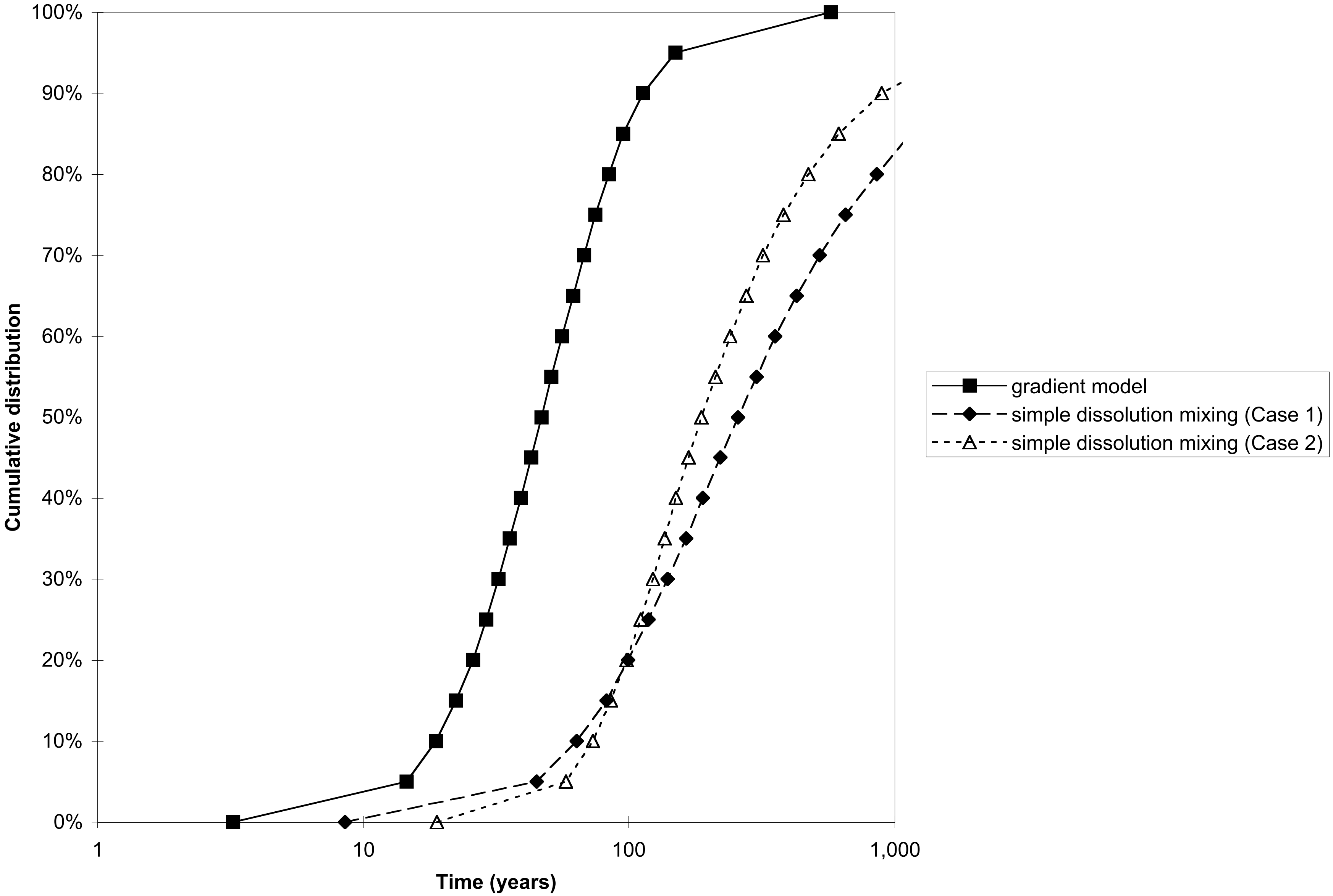

Figure B-1. Forecast cumulative distribution of free-product dissolution time.

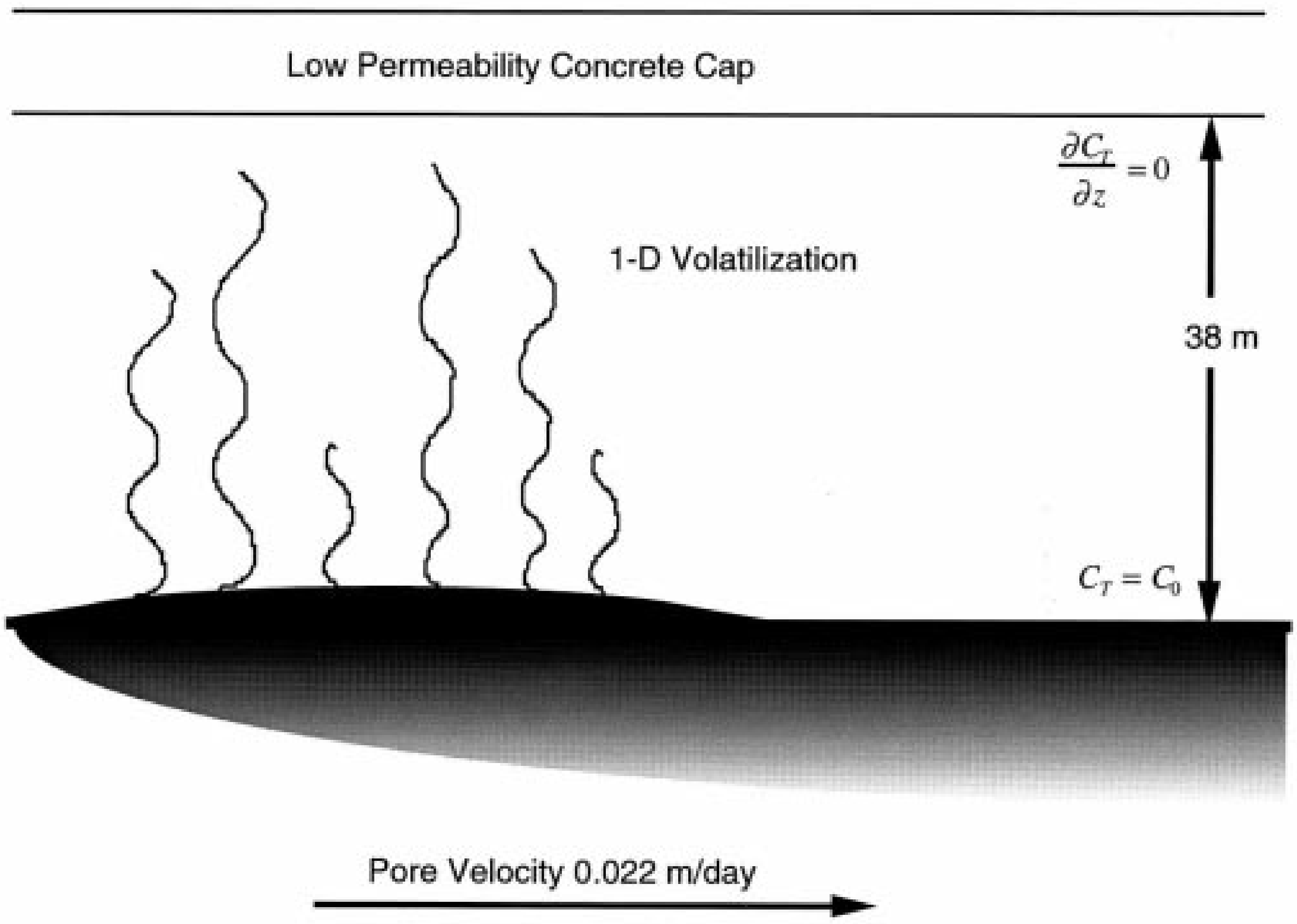

Figure B-2. Conceptual scenario of volatilization/dissolution of NAPL plume.

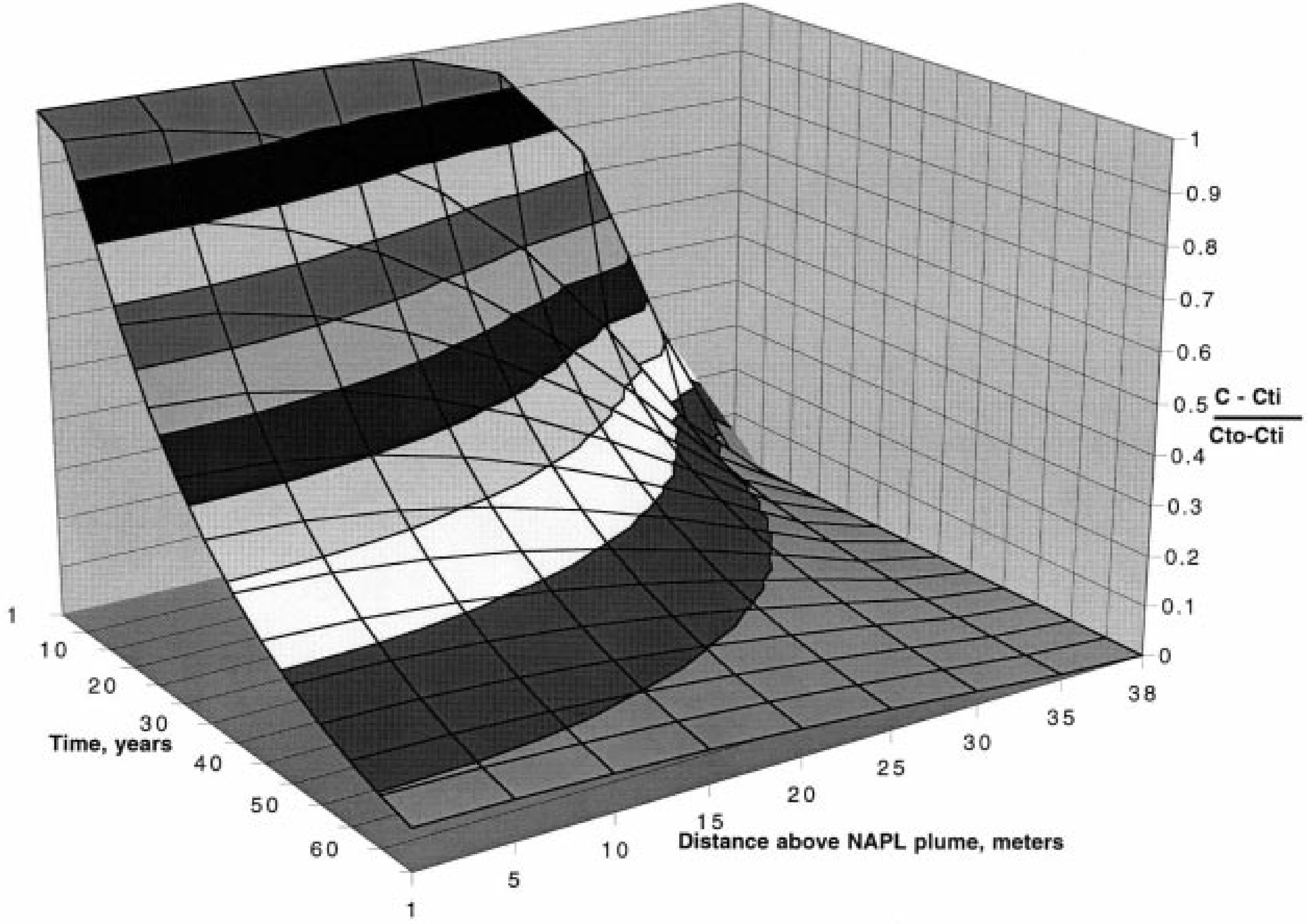

Figure B-3. 1-D diffusion of benzene vapor from a FHC NAPL to the overlying vadose zone.

Appendix C

Plume Natural Attenuation Analysis

Appendix C

Plume Natural Attenuation Analysis

C-1. Overview

As part of a natural attenuation study conducted at GAFB, a number of potential indicators of bioattenuation of the dissolved hydrocarbons have been evaluated during site investigation activities. Measured variations in dissolved concentrations of hydrocarbon constituents are not inconsistent with significant bioattenuation. However, it is very difficult to conclusively assert that the plume movement is being controlled by bioattenuation based solely on measured changes in concentration, because the sampling history does not provide sufficient temporal and spatial resolution over a sufficiently long period of time. In this case, indirect methods of evaluating plume stability, using geochemical indicators and relatively simple analytical solute transport models, may be employed to provide insight into plume stability.

C-2. Plume Length Analysis

Rice et al. (1995) noted that dissolved benzene typically stabilized in most groundwater environments, with the length of benzene plumes ranging from 100 ft. (50th percentile) to 260 ft. (90th percentile) among the sites examined. This plume length stabilization reflects a balance between dissolved contaminant mass introduced from residual sources and attenuation processes (particularly biodegradation) integrated across the plume.

To address the issue of plume stability in the special case of GAFB, Monte Carlo analyses were performed on forecast plume lengths using the analytical solution to the advective-dispersive solute transport equation provided by Domenico (1987). The two-dimensional form of this solution is,

$$C(x,y,t)=\left(\frac{C_0}{4}\right)\exp\left\{\left(\frac{x}{2\alpha_x}\right)\left[1-\left(1+\frac{4R\lambda\alpha_x}{v}\right)^{1/2}\right]\right\}erfc\left[\frac{x-\frac{vt}{R}\left(1+4R\lambda\alpha_x/v\right)^{1/2}}{2\left(\alpha_x\frac{vt}{R}\right)^{1/2}}\right]$$

$$\left\{erf\left[\frac{(y+Y/2)}{2(\alpha_y x)^{1/2}}\right]-erf\left[\frac{(y-Y/2)}{2(\alpha_y x)^{1/2}}\right]\right\} \tag{C-1}$$

where C_0 refers to the source concentration, α_x the longitudinal dispersivity, α_y the transverse dispersivity, λ the first-order decay coefficient, v the groundwater pore velocity, R the retardation coefficient, Y the width of the line source, t the monitor time, and x and y the coordinates of the monitor point relative to the source. The model used in this evaluation consisted of programming Equation (C-1) into a Microsoft Excel spreadsheet and then using the Crystal Ball add-in package (Decisioneering, Inc., 1996) for Excel to run Monte Carlo simulations using probability distributions associated with the given parameters (Table C-1).

Forecasting probable plume lengths associated with a continuous source is achieved by predicting concentrations downgradient of the source (centerline) and then using a suitable search algorithm such as bisection or Newton's method to find the location downgradient at which a certain concentration is reached. Plume length may then be defined as the distance from the source to such a location. This technique was used to generate forecast cumulative distributions of benzene plume lengths as defined by the 10 ppb contour.

The constant concentration at the line source is based on the effective solubility of benzene, C_s, which was calculated using the pure phase solubility of benzene, C_p, (1,770 mg/L) and Raoult's law approximation using the mole fraction of benzene in JP-4, X_b,

$$C_0 = C_s = C_p X_b \tag{C-2}$$

For simplicity, the line source width term in Equation (C-1) is assumed to reflect the width of the observed NAPL plume (idealized as a square), where the layer of water in immediate contact with the NAPL is assumed to be saturated with benzene to its effective solubility limit. Thus,

$$Y = \sqrt{A} \tag{C-3}$$

where A is the area of the NAPL pool. The retardation coefficient, R, is calculated through the expression,

$$R = 1 + \frac{K_{oc} f_{oc} \rho_b}{\phi} \tag{C-4}$$

where K_{oc} is organic carbon partitioning coefficient (83 mL/g for benzene), f_{oc} the organic carbon fraction of the sediment, ρ_b the soil bulk density, and ϕ the porosity.

Flow velocity is calculated for each realization in accordance with Darcy's law,

$$v = \frac{K \nabla h}{\phi} \tag{C-5}$$

In studies conducted at GAFB with an *in situ* flow meter device, Wilson et al. (1995) found that local preferential flow pathways existed within the hydrocarbon-impacted zone of the aquifer, characterized by flow velocities an order-of-magnitude higher than those calculated using Darcy's law and hydraulic conductivity estimates based upon slug tests and pumping tests. However,

Table C-1. Assumptions used in probability forecast model.

Parameter	Probability distribution	Basis
Benzene mole fraction in JP-4	Lognormal. Mean = 0.56%; standard deviation = 0.28%.	Pure benzene solubility = 1770 mg/L; Raoult's law approximation; mole fraction of benzene assumed equal to its weight fraction in JP-4, 0.5% (IT, 1996). Variations in JP-4 composition and departures from the ideality of Raoult's law may explain slightly higher concentrations of benzene noted in some GAFB groundwater samples.
K, hydraulic conductivity	Lognormal. Mean = 61.2 ft/day; standard deviation = 30.4 ft/day. Corresponds to the 10th-percentile = 30 ft/day and the 90th-percentile = 100 ft/day.	Based upon site data (IT, 1996).
∇h, hydraulic gradient	Lognormal. 25th percentile = 0.002; 75th-percentile = 0.003.	Based upon site data (IT, 1996).
ϕ, porosity	Normal. Mean = 0.25; standard deviation = 0.03.	Postulated.
f_{oc}, fractional organic carbon content	Lognormal. Mean = 0.08%; standard deviation = 0.29%. Corresponds to the 5th-percentile = 0.02% and the 95th percentile = 0.29%.	Based upon site date (IT, 1996).
λ, decay coefficient	Lognormal. Mean = 0.86% day^{-1}; standard deviation = 2.0% day^{-1}.	Based on decay coefficients suggested by Wilson et al. (1995) for GAFB. Also consistent with Buscheck et al. (1996).
α_x ratio (ratio of longitudinal dispersivity to plume length scale, *vt*)	Lognormal. Mean = 0.13; standard deviation = 0.10 (median = 0.10).	Postulated (based on the standard assumption that $\alpha_x \sim$ 10% plume length).
α_y ratio (ratio of transverse dispersivity to longitudinal dispersivity)	Lognormal. Mean = 0.13; standard deviation = 0.10 (median = 0.10).	Postulated (based on the standard assumption that $\alpha_y \sim$ 10% $\times\ \alpha_x$).
t (time elapsed between introduction of source and groundwater quality sample)	Normal. Mean = 27 years (10,000 days); standard deviation = 5.4 years(20% of mean; truncated at 30 years). Doubled for projection in year 2022.	Postulated (assuming source became active in late 1960s).
A (area of NAPL pool)	Normal distribution. Mean = 1,860,000 ft^2; standard deviation = 186,000 ft^2 (assumed to be equal to 10% of the mean for simplicity).	IT (1996).

these high permeability zones were found to be only on the order of 2 ft in thickness, so thecontinuity of such features over large lateral distances is questionable. It is likely, in an alluvial environment such as that of GAFB, that such high permeability features would tend to appear and then pinch out again frequently across the aquifer. Groundwater flow lines would tend to converge into such features and then disperse again once a pinch out is encountered. As a result, megascopically-averaged flow velocities over large distances in the subsurface would be likely to approach those suggested by aquifer tests.

Nevertheless, to address this concern, separate forecast scenarios were run for the distribution of hydraulic conductivity given by aquifer testing (30 ft/day to 100 ft/day), and for higher values representative of preferential subsurface flow pathways (300 ft/day to 1,000 ft/day, also assuming a lognormal distribution). The results are shown on Figure C-1 for 1995 and 2022. Two observations emerge from this analysis: 1) lower hydraulic conductivity values produce more realistic estimates of present benzene plume length (on the order of 4,000 ft for the 50th percentile; within an order-of-magnitude of the approximate current downgradient extent of the GAFB plume) than do the higher estimates (on the order of 30,000 ft), and 2), for both scenarios, forecast plume lengths do not change appreciably with time (i.e., plume has become stable regardless of flow velocity). These results, taken together, suggest that the higher flow velocities measured by Wilson et al. (1995) do not necessarily imply that the GAFB plume will continue to grow, assuming an adequate supply of sulfate and other electron acceptors.

Sensitivity analyses of the simulation results suggest that uncertainty in the degradation rate has the greatest impact in plume length, followed by hydraulic conductivity, gradient, dispersivity, and fractional organic content.

C-2.1. Mass Balance Analysis of Plume Stability

As described above, a simple plume model assuming a continuous source and a first-order decay relationship can be used to gain insights into the stability of a contaminant plume. As second, independent means for analyzing plume stability consists of a mass balance analysis, which attempts to quantify the rates of contaminant input into groundwater (in this case, through NAPL dissolution), and the rate of contaminant loss (through degradation).

The rate of contaminant (i.e., dissolved benzene) input into the groundwater can be estimated by integrating dissolution fluxes calculated in Appendix B (i.e., Equation B-3) across the estimated surface area of the NAPL pool. Assuming a solute flux of 1.82×10^{-3} g/m^2/day (the median value yielded in the Monte Carlo dissolution analysis) and a contact area of 1,860,000 ft^2, the total mass of benzene dissolving into groundwater would be equal to approximately 310 g/day. It is highly likely that this number is extremely conservative because 1) dissolution fluxes out of the NAPL pool will decrease over time and 2) volatilization will deplete benzene and other volatiles even more rapidly than dissolution (see Appendix B). Nevertheless, using this conservative solute flux estimate, and a first-order decay coefficient of approximately 0.80% day^{-1} (Wilson et al., 1995), a total mass of 39.2 kg of dissolved benzene in groundwater would be needed to maintain a net mass balance (assuming a uniform degradation rate).

Assuming a simplified uniform square plume, mean concentrations of dissolved benzene associated with this mass are shown on Table C-2 over a variety of spatial scales. Variability includes different plume depths and area size factors relative to the NAPL pool area (assuming a uniform porosity of 25%). In general, given the observed spatial extent and depth of the benzene plume at GAFB, and the observed benzene concentration distributions, the results suggest that assertion of plume stability appears to be quite reasonable purely from a mass balance viewpoint.

Table C-2. Mean concentrations of BTEX implied by mass balance arguments.

Plume depth (m)	Size factor	Contaminated volume (m^3)	Implied mean concentration (g/m^3)	Implied mean concentration (ppb)
0.1	1	4.32×10^3	9.08	9,080
0.5	1	2.16×10^4	1.82	1,816
1	1	4.32×10^4	9.08×10^{-1}	908
2	1	8.64×10^4	4.54×10^{-1}	454
5	1	2.16×10^5	1.82×10^{-1}	182
0.1	2	8.64×10^3	4.54	4,540
0.5	2	4.32×10^4	9.08×10^{-1}	908
1	2	8.64×10^4	4.54×10^{-1}	454
2	2	1.73×10^5	2.27×10^{-1}	227
5	2	4.32×10^5	9.08×10^{-2}	91
0.1	4	1.73×10^4	2.27	2,270
0.5	4	8.64×10^4	4.54×10^{-1}	454
1	4	1.73×10^5	2.27×10^{-1}	227
2	4	3.46×10^5	1.13×10^{-1}	113
5	4	8.64×10^5	4.54×10^{-2}	45

C-3. Reactive Transport Analysis of Geochemical Indicators

Geochemical indicators of bioattenuation have been measured in groundwater at GAFB as part of the natural attenuation study (IT, 1996). These parameters include dissolved oxygen, nitrate, sulfate, manganese, iron, methane, bicarbonate (as total alkalinity), pH, and Eh. Different biologically-mediated oxidation reactions may be associated with each of the principle electron acceptors available (i.e., oxygen, nitrate, sulfate, manganese, iron). For example, Bradley et al. (1992) found clear evidence of biodegradation of JP-4 components through denitrification processes in a shallow aquifer. To gain insights into the integration of various biogeochemical regimes with transport processes in groundwater at GAFB, a semi-analytical reactive transport model was employed to simulate the chemical evolution of the impacted aquifer over time. The model used for this purpose couples an analytical solution to the advective-dispersive transport equation with a geochemical speciation model (McNab, 1996). The geochemical speciation model uses mass conservation and thermodynamic constraints to estimate changes in water chemistry parameters resulting from equilibration reactions. The analytical transport model uses the two-dimensional solution of Domenico (1987) to simulate the movement of a contaminant undergoing decay with a continuous line source approximation.

Using a set idealized hydrologic and chemical parameters characteristic of the GAFB site (Table C-2), the evolution of the local geochemical environment in association with the degrading hydrocarbon plume was simulated over a period of 10,000 days (approximately 27 years); a period of time roughly consistent with the release history at the site. For simplicity, the dissolved hydrocarbon plume was represented chemically by toluene, C_7H_8, with a constant source area concentration of 40 mg/L (depth-averaged).

Comparisons between measured indicator data and simulated plume evolution are shown on Figures C-2 through C-11 for the various parameters (groundwater flow direction is approximately north). In general, model predictions are qualitatively consistent with observed changes in indicator parameters in association with the hydrocarbon plume (Fig. C-2). These changes include locally depleted dissolved oxygen, nitrate, and sulfate concentrations (Figs. C-3 through C-5, respectively), local generation of methane (Fig. C-6), local mobilization of manganese and iron due to biodegradation/thermodynamic undersaturation of manganese and ferric iron oxides (Figs. C-7 and C-8, respectively), locally-depleted Eh (Fig. C-9), locally-increased inorganic carbon as bicarbonate as a result of hydrocarbon mineralization (Fig. C-10), and a local decrease in pH (Fig. C-11). These simulation results suggest in a qualitative manner how observed spatial changes in inorganic geochemistry noted at GAFB may be explained in a consistent manner by bioattenuation reactions.

Table C-3. Reactive transport modeling parameters.

Pore velocity	**2.2×10^{-2} m/day**
Longitudinal dispersivity (postulated)[1]	**80 m**
Transverse dispersivity (postulated)	**10 m**
Source concentration	**40 mg/L**
Source width	**50 m**
Mean toluene half-life (postulated)[2]	**300 days**
Background pH	**7.6**
Background Eh	**770 mV**
Background O_2	**8 mg/L**
Background HCO_3^-	**230 mg/L**
Background NO_3^-	**2 mg/L**
Background SO_4^{2-}	**170 mg/L**

Differences in major hydrocarbon geochemical indicator parameters between the hydrocarbon plume and background groundwater composition are shown on Figure C-12 for both measured data and simulation results. For both the field data and the model results, the hydrocarbon plume is defined for this analysis as characterized by water composition with total BTEX greater than 1 ppm, while background is defined as total BTEX less than 0.1 ppm.

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[1] Large dispersivity values, in comparison to the scale of observation, were chosen for this analysis as conservative assumptions to account for the presence of preferential flow pathways.

[2] Conservative assumption.

Several important observations emerge from these data: 1) approximately 80 percent of the observed depletion of BTEX between plume conditions and background conditions can be accounted for stoichiometrically in the accumulation of inorganic carbon (bicarbonate), which is indicative of hydrocarbon mineralization, 2) observed net changes in average concentration of the major electron acceptors accounts for approximately 2.7 times the observed generation of bicarbonate. This indicates that biologically-mediated oxidation of the hydrocarbons (primarily by sulfate reduction) can easily account for the observed transformation of the hydrocarbons into inorganic carbon (the apparent loss of a significant portion of the inorganic carbon may be due to offgassing of CO_2), and 3) when comparing observed changes in indicator parameters to those predicted by the model, it is apparent that the model is actually conservative in estimating the amount of dissolved hydrocarbon that is biodegraded in the center of the plume (e.g., methanogenesis and sulfate reduction are underestimated; inorganic carbon production is underestimated).

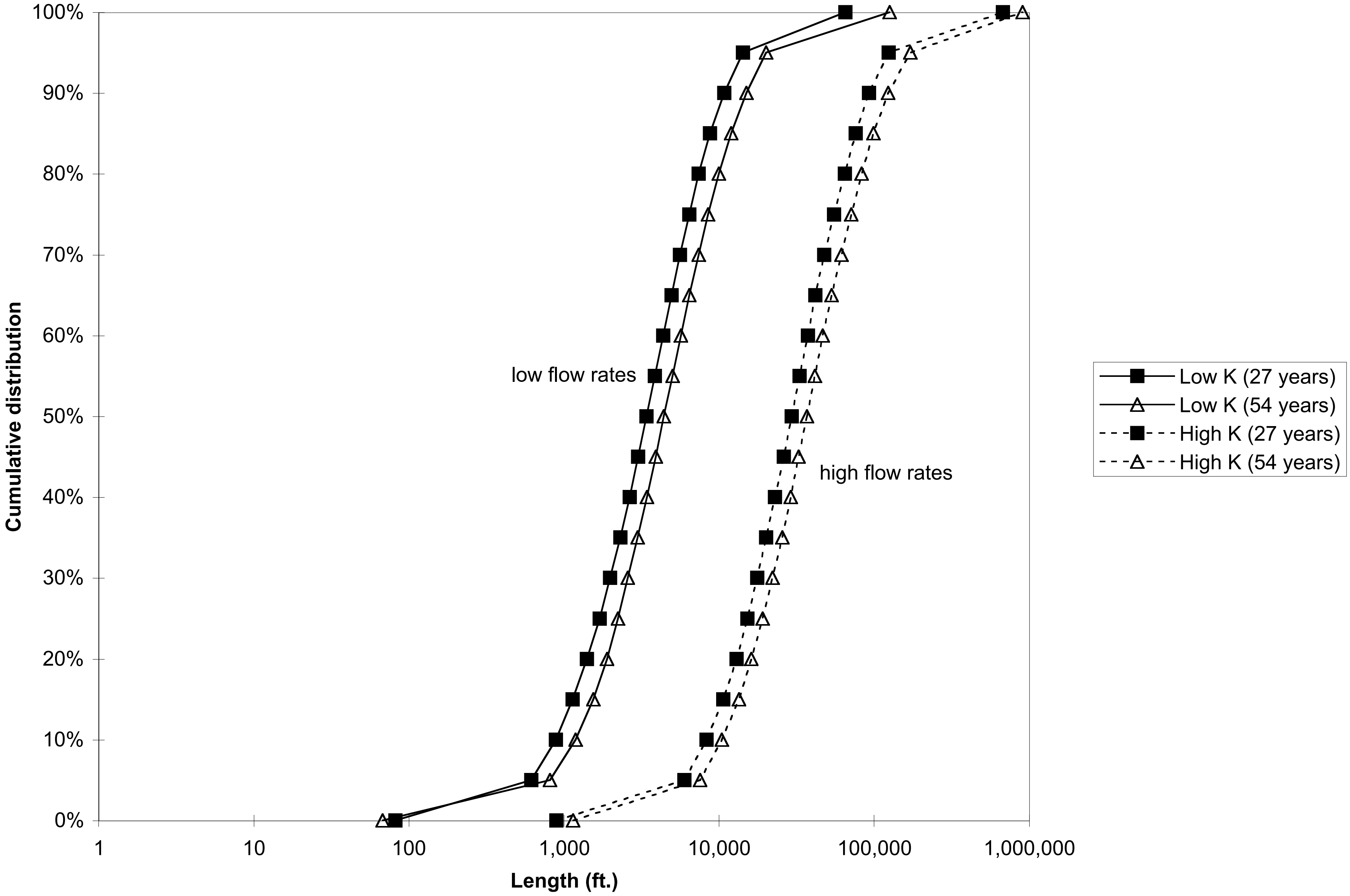


Figure C-1. Forecast idealized benzene plume lengths for low and high hydraulic conductivity test cases.

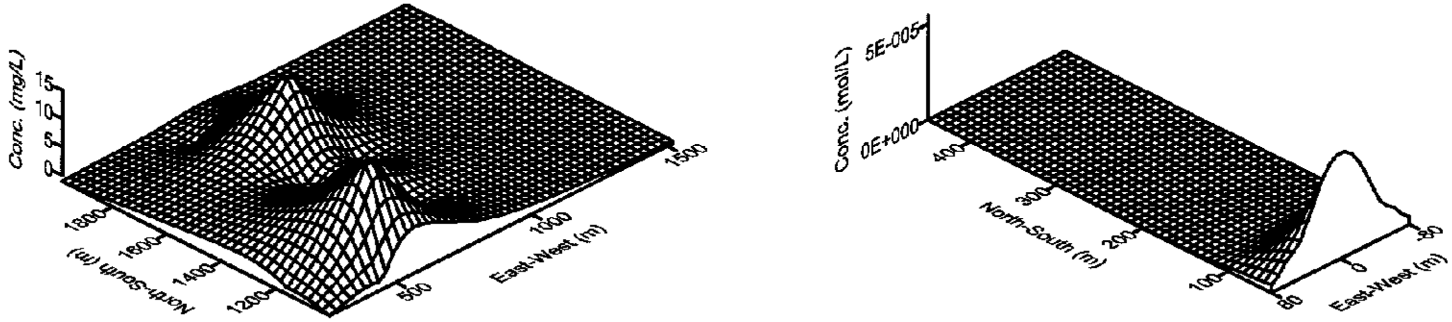


Figure C-2. Dissolved hydrocarbon - measured total BTEX (left, mg/L) and simulated toluene (right, mol/L).

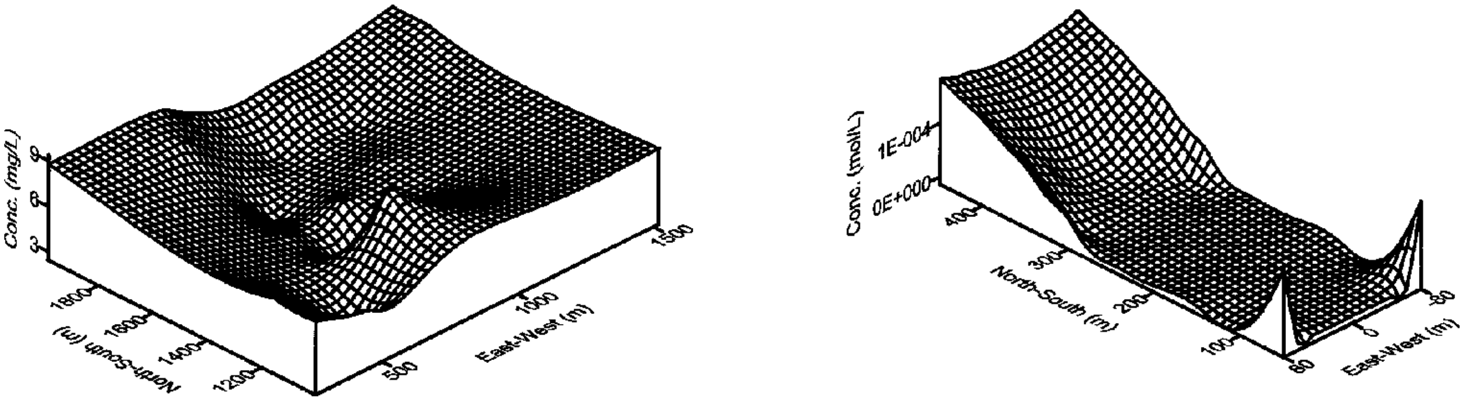


Figure C-3. Dissolved oxygen - measured (left, mg/L) and simulated (right, mol/L).

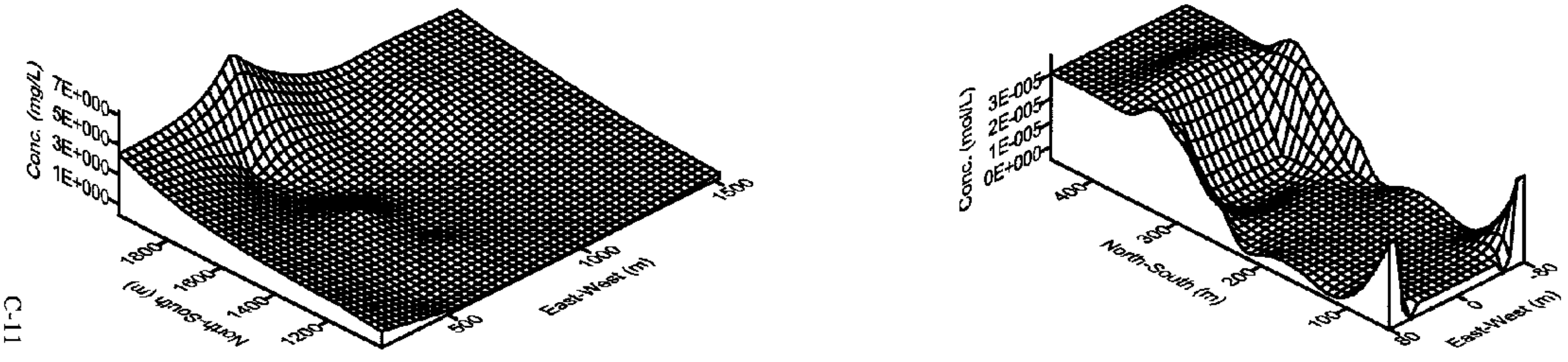


Figure C-4. Nitrate - measured (left, mg/L) and simulated (right, mol/L).

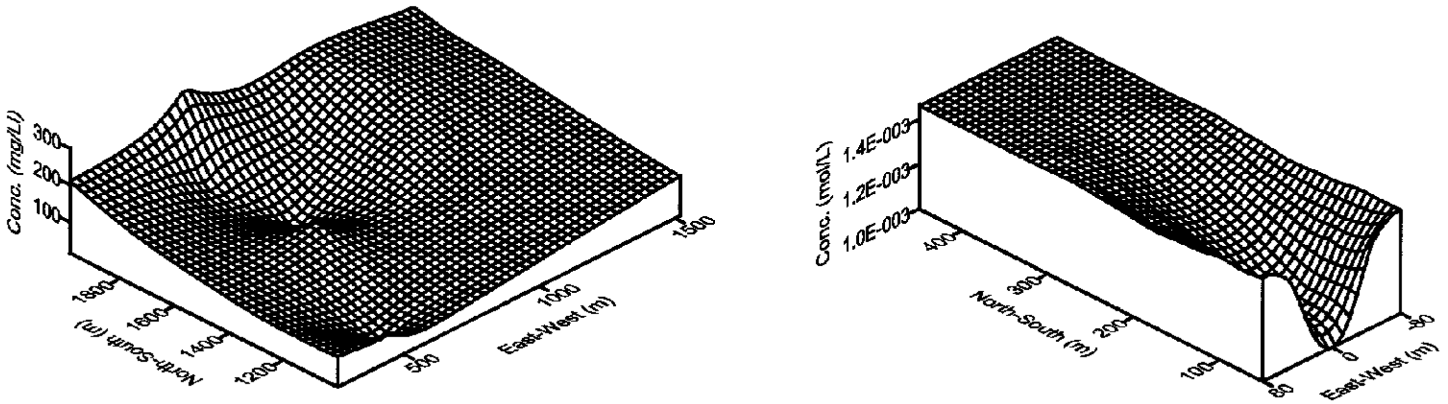


Figure C-5. Sulfate - measured (left, mg/L) and simulated (right, mol/L).

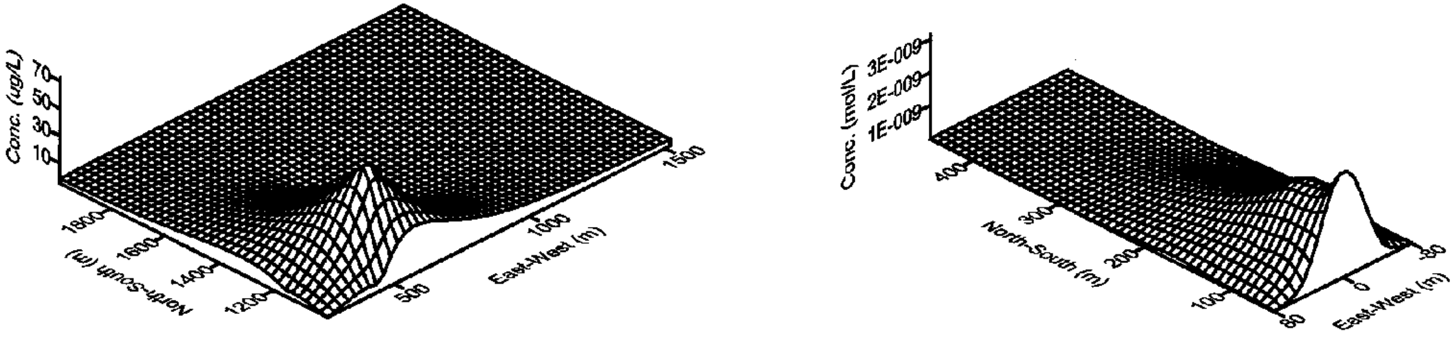
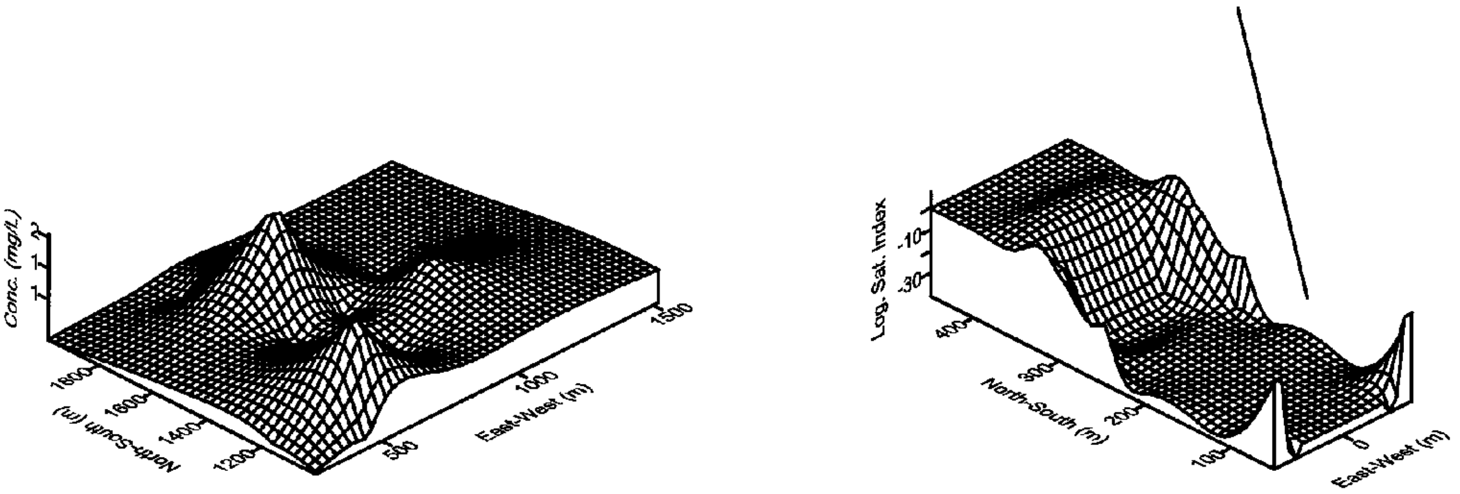


Figure C-6. Methane - measured (left, micrograms/L) and simulated (right, mol/L).



Bimessite dissolution favored.

Figure C-7. Manganese - measured (left, mg/L in solution) and simulated thermodynamic saturation with birnessite (right).

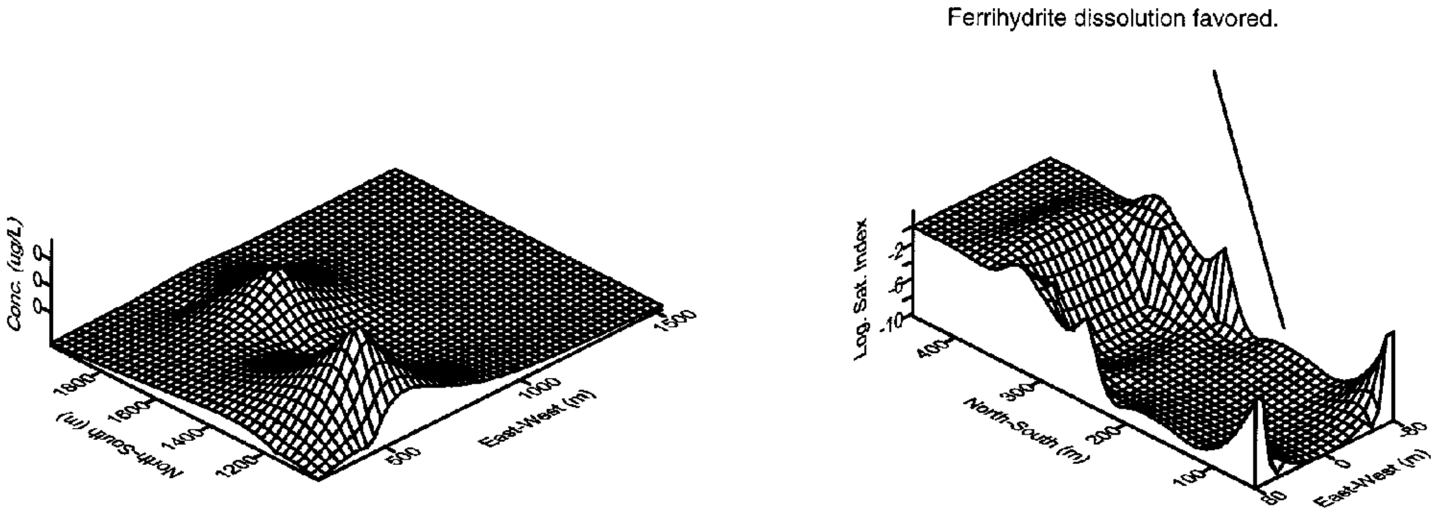

Ferrihydrite dissolution favored.

Figure C-8. Iron - measured (left, micrograms/L in solution) and simulated thermodynamic saturation with ferrihydrite (right).

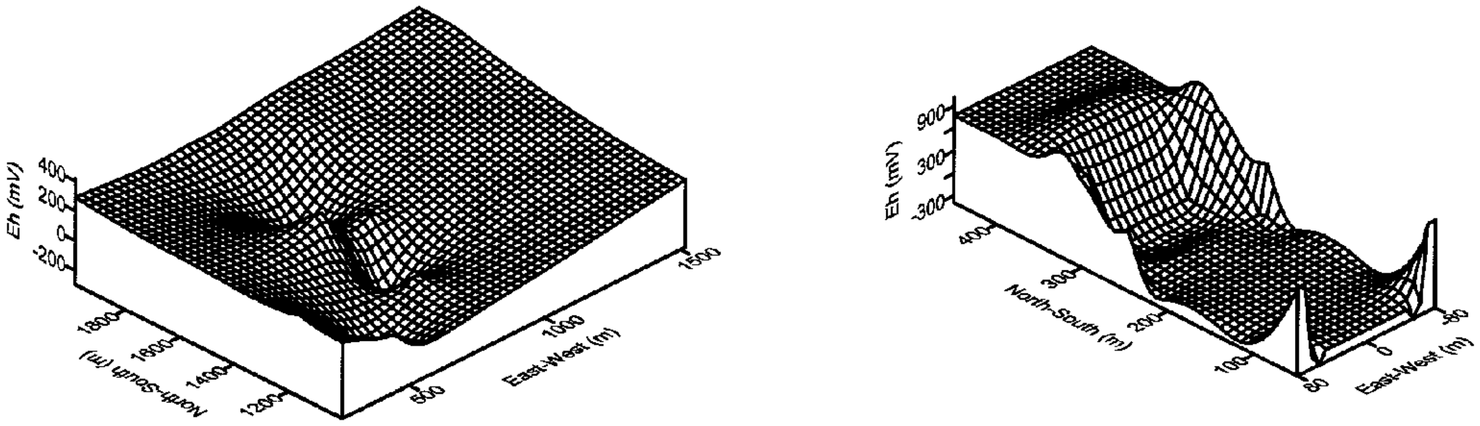


Figure C-9. Eh - measured (left) and simulated (right), millivolts.

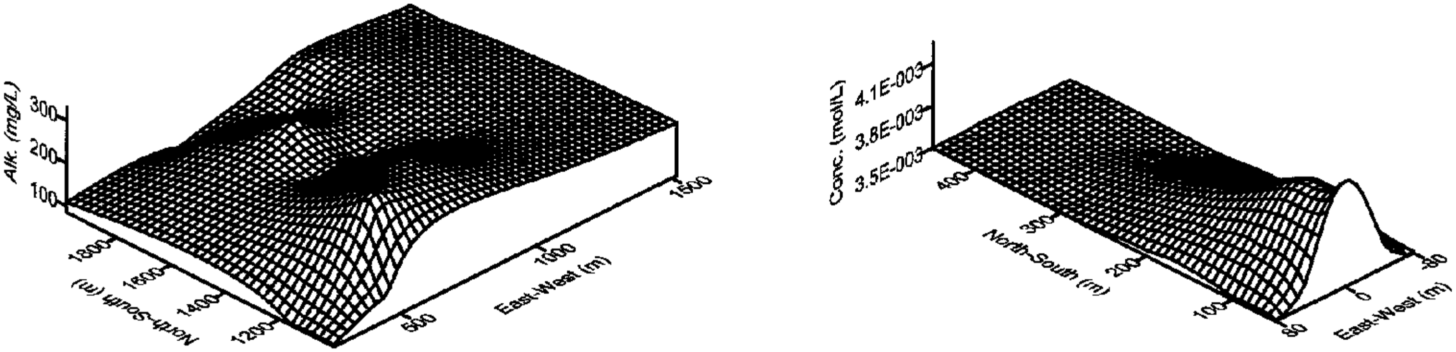


Figure C-10. Bicarbonate - measured (left, mg/L CaCO3 bicarbonate alkalinity) and simulated (right, mol/L).

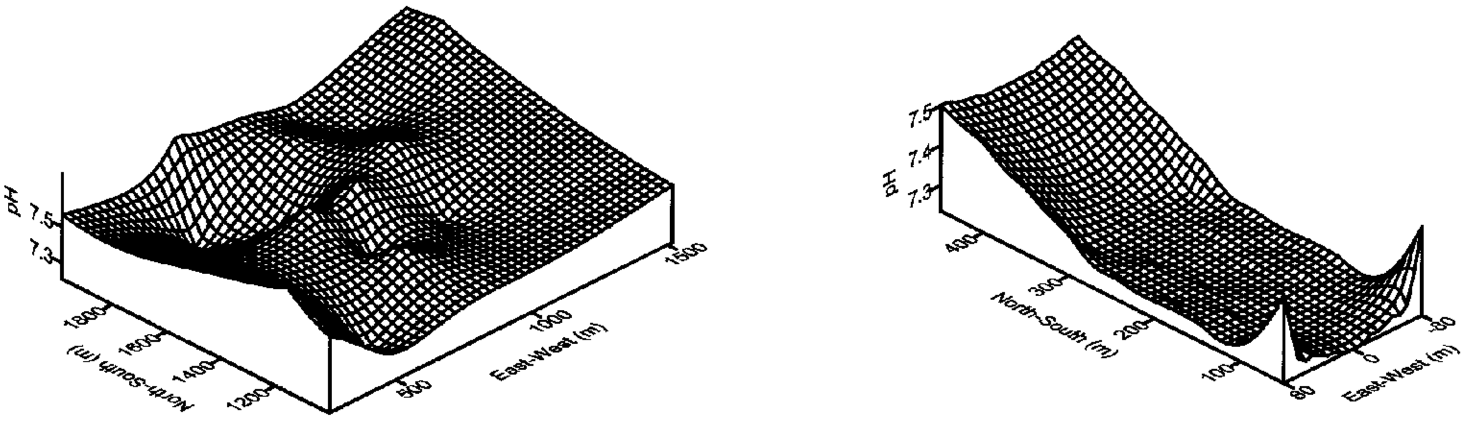


Figure C-11. pH - measured (left) and simulated (right).

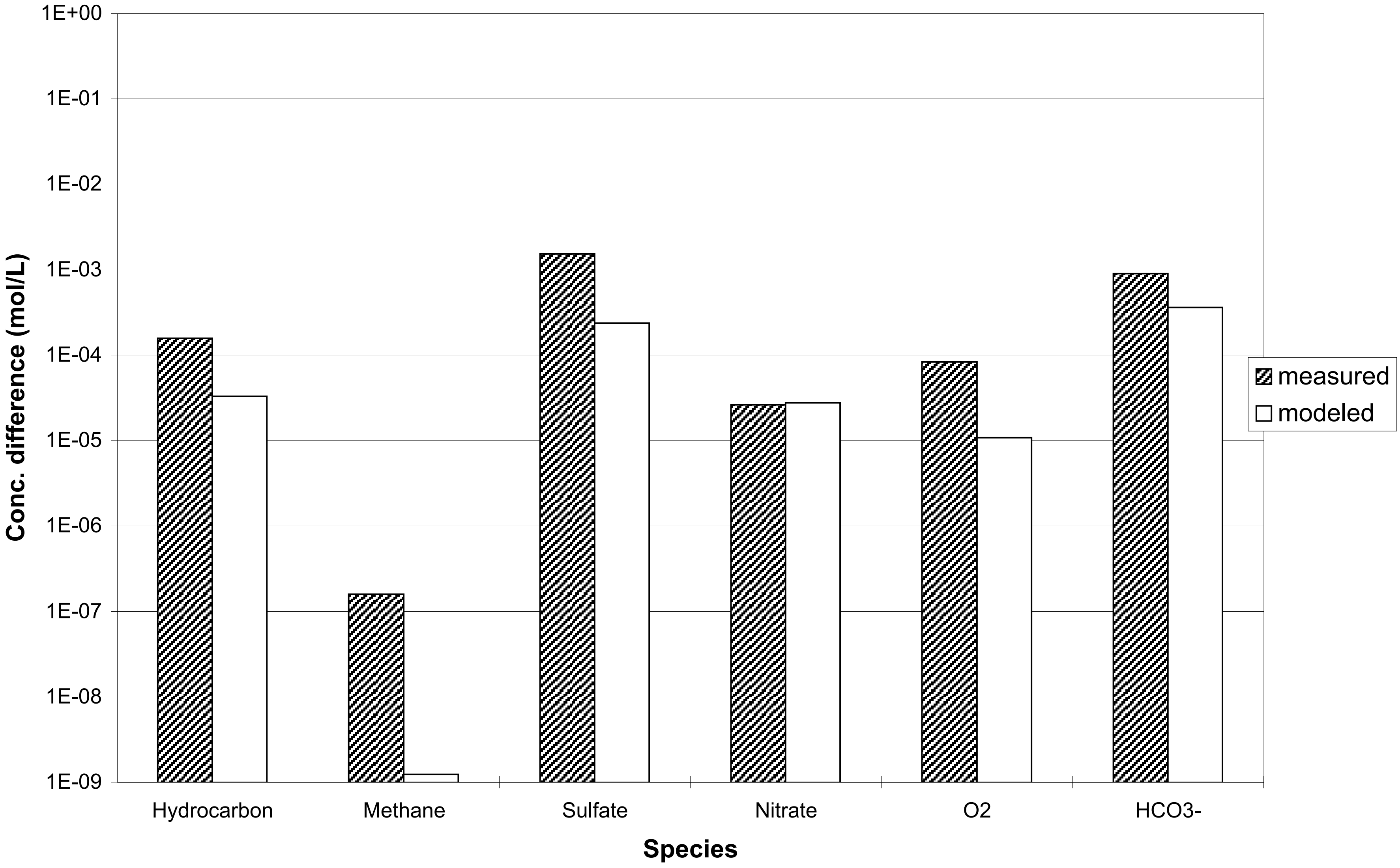


Figure C-12. Electron acceptor variations due to bioattenuation (measured and modeled).

Appendix D

Inhalation Risk

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Inhalation Risk

The inhalation risk at the surface was evaluated using a one-dimensional diffusive transport model for flux through the vadose zone. The volatile flux of chemicals in a one-dimensional (1-D) porous media have been assessed by Jury et al. (1983; 1984a,b,c; 1990) using an analytical modeling approach. Factors taken into account included degradation, as well as an effective water solute velocity; the latter which may be used to assess sites with either leaching, evapotranspiration, or no water movement through the subsurface. At GAFB, evapotranspiration is expected to far exceed that of the yearly recharge. However, due to the extreme depth of the groundwater zone, at 38 meters below the surface, evapotranspiration is not a likely factor in the transport of volatile components. Therefore, the version of the Jury model presented here does not take this process into account.

According to Jury et al. (1990), the cumulative flux at the surface, assuming a zero boundary layer thickness, can be expressed as:

$$V_c^b(\infty) = C_o H \left(\frac{D_E}{\lambda}\right)^{1/2} \exp\left[-L\left(\frac{\lambda}{D_E}\right)^{1/2}\right]\left\{1 - \exp\left[-W\left(\frac{\lambda}{D_E}\right)^{1/2}\right]\right\} \qquad \text{(D-1)}$$

where $V_c^b(\infty)$ is the cumulative vapor flux (g·cm/L), C_o is the concentration of the volatiles diffusing from the separate phase FHC product (g/L), L the depth to the NAPL, W the thickness of the NAPL, λ the degradation rate (1/sec), and D_E is the effective diffusion coefficient as defined by:

$$D_E = \frac{\theta_g^{10/3} D_g H + \theta_l^{10/3} D_l}{\varphi^2\left(\rho_b f_{oc} K_{oc} + \theta_l + \theta_g H\right)} \qquad \text{(D-2)}$$

where the equation parameters are as defined in Appendix B. D_l is the diffusion coefficient of the volatile component in water.

The target risk level associated with the above, is

$$TR = \frac{C_g \quad CPF \quad IR \quad EF \quad ED}{BW \quad AT \quad 365\, d/yr} \qquad \text{(D-3)}$$

where CPF refers to the cancer potency factor, IR is the inhalation rate of air, EF is the exposure frequency, ED is the exposure duration, BW is adult average body weight, and AT is the averaging time, as seen in Table D-1.

Since Equation D-1 reflects the cumulative flux over an infinite time period, it must be divided by the averaging time, *AT*, as well as a mixing zone height, *d*, taken here to be 2 m, to give the yearly average concentration. This gives:

$$C_g = \frac{V_o^b(\infty)}{AT \;\; d} \tag{D-4}$$

A series of Monte Carlo simulations, utilizing Crystal Ball (1993) in a manner similar to that described for plume length simulation in Appendix C, were used to address the above aspects. Two different simulation sets were performed using two different degradation rate distributions. The two simulation scenarios chosen involve the worst case scenario at the site, where the NAPL FHC was five feet (~1.5 m) in thickness, and addressed the risk associated with a large potential source. The second set of simulations addressed the issue of variable source thickness *W*, where the thickness was varied using a lognormal distribution with a 1st percentile thickness *W* of 1 cm up to a 99th percentile *W* of 1.5 m, and represents the best site-wide estimate of the risk. Each of these simulations were analyzed under two differing degradation rates. These two scenario and rate distributions are shown in Table D-1.

The first degradation rate chosen is the same used for the groundwater flow analysis of Appendix C, where the range is $\lambda = f(\mu = 9.95 \times 10^{-8}/\text{s}, \sigma = 2.31 \times 10^{-7}/\text{s})$. This range was based on decay coefficients suggested by Wilson et al. (1995) for GAFB and are consistent with those seen by Buscheck et al. (1996).

The second degradation rate of $\lambda = f(\mu = 9.95 \times 10^{-7}/\text{s}, \sigma = 2.31 \times 10^{-6}/\text{s})$ was chosen assuming that degradation rates will not be as oxygen limited as in the saturated zone. Both degradation rate distributions are shown in Figure D-1.

Due to the high atmospheric flux potential at GAFB, degradation rates in the vadose zone are not as oxygen limited as those in groundwater. Degradation of volatiles in the vadose zone takes place primarily in the water phase; both oxygen and the volatile FHC components easily dissolve into the water surface film surrounding the soil particles. Since oxygen is much more freely available in the vadose zone than in groundwater, the overall degradation rates are likely to be higher than those found in groundwater.

Howard (1991) reports ranges of degradation rates in soil with a distribution that may be represented by $\lambda = f(\mu = 7.72 \times 10^{-7}/\text{s}, \sigma = 1.93 \times 10^{-7}/\text{s})$, which has a similar mean but a much smaller standard deviation than the second degradation rate distribution chosen. DeVaull et al. (1996), in a literature survey found no degradation rate reported that was less than 5×10^{-7}/s for degradation in vadose zone type soils. Thus, the lower degradation rate distribution presented may be considered to be of a low likelihood, while the higher degradation rate distribution may be considered to be of a much higher likelihood.

For the worst case scenario using the lower degradation rate, the median risk level for the inhalation pathway was found to be a 4×10^{-5} excess lifetime cancer risk, with the 90th percentile equal to 4×10^{-3}. For the site-wide best estimation risk, the median was found to be 2.5×10^{-6} with a 90th percentile of 2.4×10^{-4}. For the higher degradation rate worst case scenario, the median risk level is well below 10^{-6}, with a 90th percentile risk level of 1.7×10^{-3}. The site-wide best estimation distribution has a 90th percentile of approximately 10^{-6}. Both sets of cumulative distributions are shown in Figure D-2.

It should be noted that the above calculations are for a 1-D flux under the influence of an infinite mass transfer coefficient at the ground surface. In reality, the risk is much lower due to the near zero flux condition imposed by the asphalt/concrete cap and the three-dimensional aspect of the diffusion of the volatile FHCs. Hence, the above results for the infinite mass transfer boundary condition should be considered very conservative.

Table D-1. Inhalation reisk modeling parameters.

Parameter	Probability distribution	Basis
Body Weight (BW)	Normal. m = 71 kg; s.d. = 15.9 kg	Brainard and Burmaster (1992)
Exposure Duration (ED)	Lognormal. m = 3.49 yr.; s.d. = 6.84 yr	Israeli and Nelson (1992)
Exposure Frequency (EF)	Triangular. 180, 340, 365	See explanation in text (best professional judgment)
Inhalation Rate (IR)	Lognormal. m = 12.06 L/day; s.d. = 2.55 L/day	Layton (1993)
Cancer Potency Factor (CPF) of Benzene	Point. 0.10 kg day/mg	Proposition 65
Averaging Time (AT)	Point. 70 yr	U.S. EPA (1989)
Distance to receptor (L)	Point. 38 m	Vadose zone depth
Chemical concentration (C_0)	= 1,770 × 0.005	Based on solubility limit and Raoult's Law
Source Thickness (W)	Lognormal.	See explanation in text (best
Worst case scenario	m = 1.5 m; s.d. = 0.15 m.	professional judgment)
Site wide	m = 21.9 cm; s.d. = 32.4 cm	
Air Mixing Zone Height (d)	Point. 6 ft (183 cm)	U.S. EPA (1989); Johnson et al. (1989)
Porosity (φ)	Normal. m = 0.37; s.d. = 0.042	Jury (1985)
Volumetric Water Content (θ_l)	Lognormal. m = 0.04; s.d. = 0.04 $\theta_l \le \varphi$	Based on site data (IT, 1996b)
Volumetric Air Content (θ_g)	Function of water content and porosity -$\theta_g = \varphi - \theta_l$	Function
Diffusivity (D_g) of Benzene in air	Point. 9.3×10^{-2} cm^2/s	ASTM (1995)
Diffusivity (D_l) of Benzene in water	Point. 1.1×10^{-5} cm^2/s	ASTM (1995)
Henry's Law Constant (H) of Benzene	Point. 0.223 (dimensionless)	ASTM (1995)
Organic carbon content (f_{oc})	Lognormal. m = 0.08%; s.d. = 0.29%	Based on site data (IT, 1996b)
Bulk soil density	Normal. m = 1.65 mg/kg; s.d. = 0.05 mg/kg	Jury (1985)
Degradation rate (λ)	Lognormal.	Best professional judgment;
Low likelihood	m = 9.95×10^{-8}/s, s.d. = 2.31×10^{-7}/s;	Howard (1991)
High likelihood	m = 9.95×10^{-7}/s, s.d. = 2.31×10^{-6}/s	DeVaull et al. (1996)

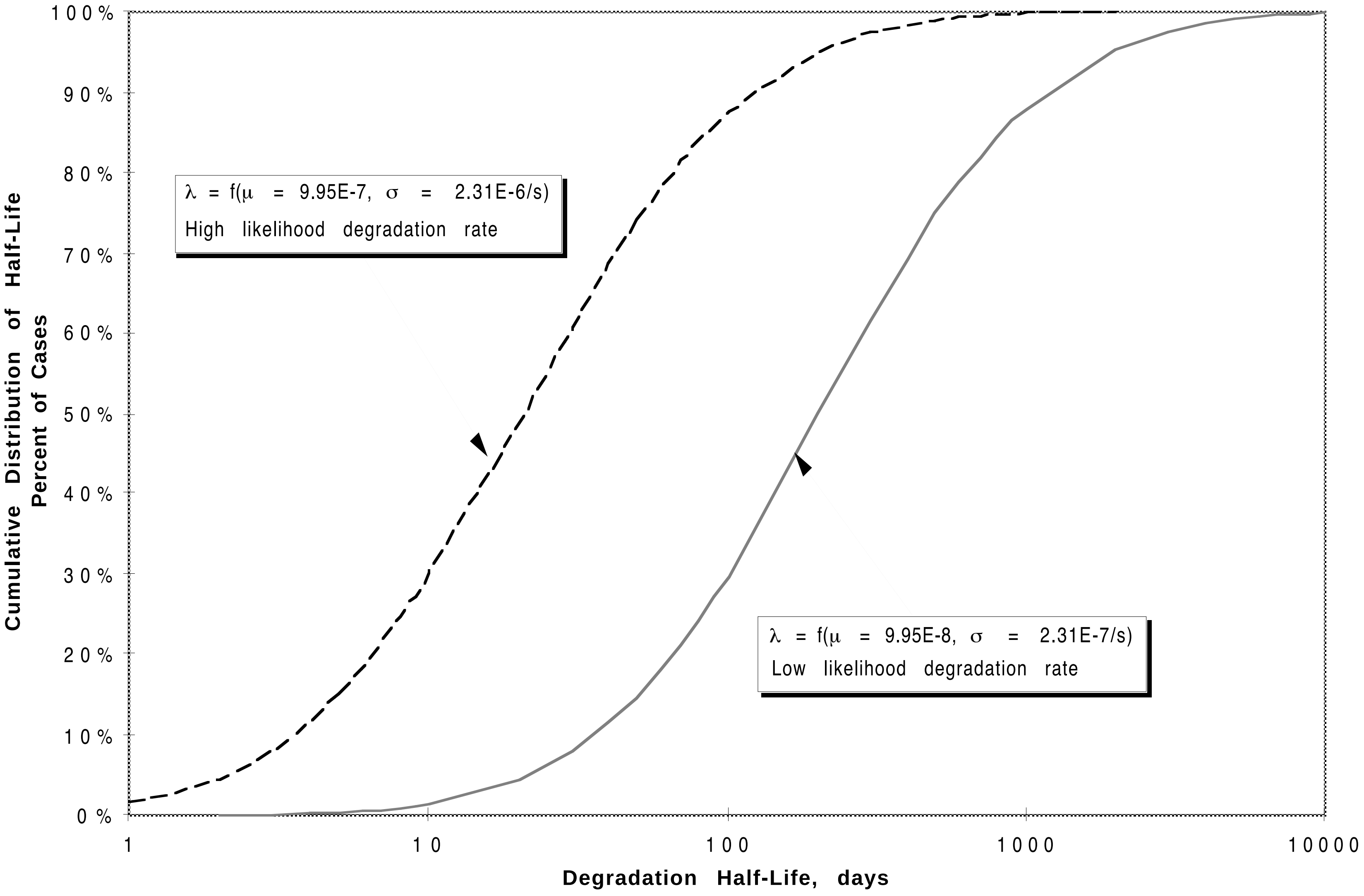

Figure D-1. Cumulative distribution of degradation half-lives for benzene as used in this model.

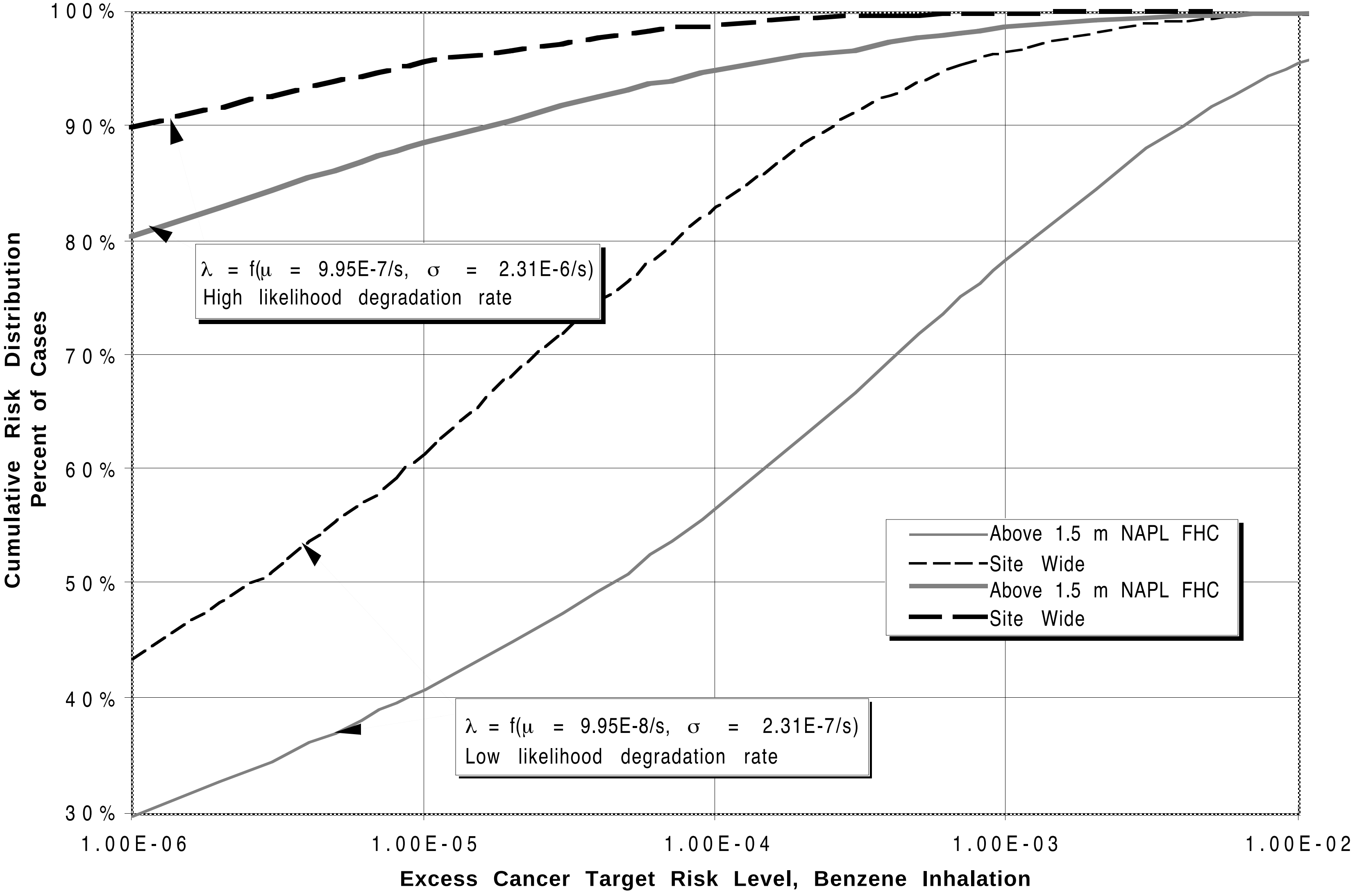

Figure D-2. Cumulative distribution of lifetime excess cancer risk for benzene inhalation at GAFB, with two different degradation rates and two different sources.

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