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UCRL-AR-129152

Risk-Based Assessment of Appropriate Fuel Hydrocarbon Cleanup Strategies for Presidio at San Francisco, Building 637 Area

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Submitted to the U.S. Army Corps of Engineers
Sacramento District, Sacramento, California

April 1998

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1. Program Overview

1.1. Introduction

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*.

1.2. LUFT Demonstration Cleanup Program

1.2.1. Background

One of the important recommendations of the original study was to identify a series of LUFT demonstration sites and to form a panel of experts comprised 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 U.S Army, Presidio of San Francisco, Building 637 area, within the San Francisco Bay RWQCB, is one of the sites selected to participate in the DoD Petroleum Hydrocarbon Cleanup Demonstration (PHCD) Program. This program will be referred to as the DoD LUFT Demonstration Cleanup Program.

The other sites selected and their corresponding RWQCB region are:

- 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:

- 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. Lorne G. Everett, UC, Santa Barbara, Hydrogeologist; Director, Vadose Zone Research Laboratory and member of LLNL/UC LUFT Team, Chief Hydrologist, Geraghty & Miller, Inc., 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. 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. Michael Kavanaugh, former Chairman, National Research Council Alternatives for Groundwater Cleanup Committee; member of The National Academy of Engineering; Vice President, Malcolm Pirnie, Inc., with expertise in evaluation of groundwater remediation alternatives and environmental decision making processes.
- Dr. Walt McNab, LLNL, Hydrogeochemist, with expertise in the evaluation of passive bioremediation processes.
- Mr. David W. Rice, LLNL, Environmental Scientist; Project Director SWRCB LUFT Re-evaluation Project; LLNL/UC LUFT Team member; DoD FHC Demonstration Program Coordinator.
- Mr. Matthew Small, R.G., U.S. EPA Region IX, Hydrogeologist; Co-Chairman of ASTM Remediation by Natural Attenuation Committee, ASTM RBCA Task Group member, U.S. EPA Monitored Natural Attenuation Committee member.

1.2.2. Risk-Based Corrective Action

The LLNL/UC recommendations report concluded that risk-based corrective action (RBCA) provides a framework to link cleanup decisions to risk. The DoD LUFT Demonstration Cleanup Program provides a series of sites where the application of a risk-based cleanup approach can be demonstrated.

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 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 pathways. 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 or 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.

1.2.3. The Appropriate Use of Passive Bioremediation

The Recommendations Report also concluded that with rare exceptions, petroleum fuel releases will naturally degrade (passively bioremediate) in California's subsurface environments. The DoD LUFT Demonstration Cleanup Program provides sites where the appropriate use of passive bioremediation can be evaluated.

Passive bioremediation can control groundwater contamination in two distinct ways:

- First, biodegradation substantially lowers the risk posed to downgradient risk receptors through plume stabilization[1].
- Second, biodegradation actively destroys fuel hydrocarbon mass in the subsurface, leading to remediation of contamination over time (e.g., eventual contaminant concentration decline and depletion of the dissolved hydrocarbon plume). From a risk-management viewpoint, the stabilization of the dissolved plume and associated reduction in exposure potential is the most important contribution of passive bioremediation.

The role of biodegradation 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 contaminant concentration data.
- Secondary evidence includes indirect indicators of biodegradation, 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.

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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 remediation 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 biodegradation, integrated across the entire spatial extent of the plume.

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 providing secondary lines of evidence, in conjunction with modeling where appropriate, may support a hypothesis for the occurrence of biodegradation. Consequently, means for assessing the role of passive bioremediation in controlling risk by secondary lines of evidence should be fully explored at such sites.

Appropriate use of passive bioremediation as a remedial alternative requires the same care and professional judgment as the use of any other remedial alternative. This includes site characterization, assessment of potential risks, comparison with other remedial alternatives, evaluation of cost effectiveness, and the potential for bioremediation to reach remedial goals. Monitoring process and contingency planning must be considered as well.

Passive bioremediation may be implemented at a given petroleum release site either as a stand-alone remedial action or in combination with other remedial actions. The need for active source removal must also be addressed on a site-by-site basis. Source removal includes removing leaking tanks and associated pipelines, and any remaining free product and petroleum fuel saturated soil, as much as economically and technically feasible. When properly used, passive bioremediation can help manage risk and achieve remedial goals.

1.2.4. The DoD LUFT Demonstration Cleanup Program Steps

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

Step 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.

Step 2: Risk-based corrective action training for DoD Petroleum Hydrocarbon Cleanup Demonstration Program (PHCDP) participants.

Step 3: Site staff and contractors prepare the data package. EC staff reviews available data and identifies data gaps needed to apply a risk-based cleanup approach.

Step 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. (See Appendix A)

Step 5: EC staff applies a risk-based cleanup approach to the Site using best available data.

Step 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.

Step 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. This document provides these recommendations. The EC will present its recommendations at an appropriate forum.

Step 8: The EC will provide a DoD LUFT Demonstration Cleanup Program overall evaluation comparing the effectiveness of risk-based cleanup approaches at each site in the program. An estimation of the cost savings using risk-based cleanup protocols will be compared to baseline approaches. An estimation of the value of the remediated water will be made.

Step 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

The Building 637 petroleum release area is part of the Presidio of San Francisco Building 600s area investigation located near Crissy Field. This area, approximately 750 ft south of San Francisco Bay, was used as a motor pool refueling station from the late 1930s until 1989, when the station was closed following the Loma Prieta earthquake. Six above-ground storage tanks (ASTs) were in use at the refueling station, including three 20,000 gallon gasoline tanks and three 5,000 gallon diesel tanks (a 250-gallon vapor recovery tank was also present). The ASTs were connected to five fuel pumping islands via underground pipelines. The ASTs, vapor recovery tank, underground piping, and fuel islands were removed in 1993 (Montgomery Watson, 1995a).

Contamination by gasoline- and diesel-range FHCs and BTEX constituents was first noted in shallow soil sampling investigation conducted in 1990 (Montgomery Watson, 1995a), especially near underground fuel supply lines. The release history and the total volume of hydrocarbon material released to the subsurface are unknown, although patterns of soil contamination appear to be associated with the former underground piping. Subsequent investigations, which included soil borings, the installation of monitor wells and piezometers, soil gas measurements, and grab groundwater analyses by cone penetrometer equipment further delineated the extent of soil and groundwater contamination. A quarterly groundwater monitoring program involving 23 monitor wells was initiated in 1994 (Montgomery Watson, 1996). Contamination is primarily limited to gasoline- and diesel-range hydrocarbons, with occasional detections of semi-volatile organic compounds (SVOCs) such as 2-methylnapthphlanene. Low levels of chlorinated hydrocarbons (e.g., 1,2-DCE, 1,1,2-TCA, 1,2-DCA, carbon tetrachloride) appear to be associated with other sources in the area.

Presently, the Building 637 area is bounded on the north by an inactive helipad, on the east by a parking lot, and on the south by a steep hillside. Most of the site is covered by pavement; surface water runoff discharges to San Francisco Bay to the north through storm drains. Following closure of the Presidio of San Francisco, the property was transferred to the National Park Service in 1994. Future land use includes the planned restoration of historical wetlands at Crissy Field to the northeast and restoration of the historical airfield directly to the north of the Building 637 site (Williams and Josselyn, 1996). The western fingers of the proposed wetlands will lie about 550 ft west of the Building 637 site, and about 300 ft to the north.

2.2. Site Conceptual Model

2.2.1. Geology and Hydrogeology

Sediments underlying the Building 637 area are characteristic of a tidal wetland/estuarine depositional environment, with coarse-grained beach and dune sands and finer-grained materials associated with lagoonal, intertidal, and marsh environments. Fill material was added during 1912 in preparation for the Pan Pacific Exposition. There may have been additional filling during the use of the site and the boundary between native deposits and fill is not immediately clear in the stratigraphy. In turn, these materials overlay serpentinite bedrock material of the Franciscan Formation.

The Building 637 area hydrostratigraphy has been delineated into five units which are pertinent to the FHC contamination problem. The uppermost zone, designated as A1, consists of sand and gravel (largely fill material) which is hydraulically unconfined and is approximately 8 to 10-ft-thick. The saturated thickness of A1 is approximately 4 ft on average, corresponding to a vadose zone thickness on the order of 4 to 5 ft. The A1 zone is underlain by the A1/A2 Aquitard, consisting of organic rich silt and clay material up to 3 to 4-ft-thick. This unit appears to be discontinuous, pinching-out altogether in some areas and displaying a moderate hydraulic conductivity. However, slight vertical hydraulic head differences across the A1/A2 Aquitard, and different directions of hydraulic gradient above and below the unit, suggest that the unit is semi-confining, so that the A1 and A2 units may be regarded as a leaky aquifers. The semi-confined A2 unit, consisting of sand with local organic-rich silt and clay lenses, underlies the A1/A2 Aquitard and ranges from 15 ft in thickness to the north to only a few inches to the south of Building 637 where it unconformably pinches out on the underlying bedrock. The A2/B Aquitard, consisting of a continuous, 3 to 7-ft-thick organic-rich silty clay unit with occasional sand lenses, underlies the A2 zone. Unlike the A1/A2 Aquitard, this unit is a more competent confining layer with low potential for hydraulic communication (Montgomery Watson, 1995b). The B Aquifer underlies the A1/B Aquitard. This confined unit consists of silty sands with local clayey sands, ranging from 45 ft in thickness to the north and pinching out against Franciscan bedrock to the south.

The hydraulic gradient is similar in units A1 and A2 in terms of direction and magnitude. Within the A1 zone, the gradient has been observed to range between 0.002 and 0.0025 ft/ft, whereas values ranging from 0.005 to 0.006 ft/ft have been associated with the A2 zone. Flow direction is to the northwest in both units. In neither unit do hydraulic head values reflect strong tidal influences, with variations between high and low tides typically on the order of ±0.1 ft or less. Seasonal influences on the gradient direction and magnitude also appear to be minor. Values of hydraulic head and gradient associated with the B zone clearly reflect its hydraulic isolation from the overlying A1 and A2 units. The B zone appears to reflect a much stronger tidal influence, with gradient ranging from 0.0013 ft/ft at high tide to 0.004 ft/ft at low tide. The mean flow direction, as indicated by the direction of gradient, is west-southwest, which is not consistent with the expected flow direction toward San Francisco Bay to the north. Artesian conditions have been encountered in several B zone wells, suggesting a significant vertical head difference between the A2 and B zones.

Pumping tests in A1 and A2 zone wells have indicated hydraulic conductivity values ranging from 27 to 45 ft/day. Assuming a sediment porosity of 0.25, these values imply groundwater pore velocities on the order of 0.2 to 1.1 ft/day.

2.2.2. Distribution of Contaminants

Analyses of groundwater samples in the Building 637 area have included total petroleum hydrocarbons (TPH) as gasoline-range (TPH-g) or diesel-range (TPH-d) compounds, BTEX, and SVOCs. Although TPH analyses are non-compound-specific and generally do not have associated action levels in groundwater, they appear to offer the best choice for delineating the FHC plume at the Building 637 site where detections of BTEX are sporadic. However, the non-specific nature of the analysis can lead to false positive detections by identifying naturally occurring organic constituents in groundwater. To address this issue, Montgomery Watson introduced a silica gel cleanup procedure starting in July 1995, which removed biogenic polar organic compounds from the analysis. This procedure reduced the concentrations reported by the TPH analyses.

FHCs have been detected in primarily in A1 zone wells, with sporadic detections in A2 zone wells. FHCs do not appear to impact groundwater in the B zone. Within the A1 zone, a north-northwest trending gasoline (TPH-g) plume exists from the source area out to approximately 600 ft downgradient (as defined by the 100 ppb contour), with maximum concentrations detected in monitor well W-637-26 (3,700 ppb in October 1996). A diesel-range TPH plume is also evident in the A1 zone, although it is less extensive is size, ranging to approximately 360 ft downgradient of the source area. Detections of BTEX constituents have been sporadic in wells near the original release area, with no detections in downgradient wells. In the A2 zone, FHCs (both TPH-g and TPH-d) have been detected consistently only in monitor wells W-637-01R and W-637-19. BTEX components have been observed only in a limited area near B-639. Because detections in A2 wells have been sporadic and inconsistent, contouring of the FHC plume is not useful. Chlorinated hydrocarbons (1,2-DCE and VC) detected in wells 637-13 and 637-19 appear to be from a separate source. In B zone wells and in a cone penetrometer survey of B zone sediments, low levels of diesel-range hydrocarbons were inconsistently reported by TPH analyses. Subsequent analyses with silica gel cleanup confirmed the absence of FHCs. As a result, exclusion of B zone wells from the groundwater monitoring program has been approved by RWQCB (Montgomery Watson, 1996). Benzene concentrations have been observed between 2.8 and 84 μg/L in the A1 Zone area and from 0.6 to 390 μg/L in the A2 zone.

3. Risk Analyses and Management

3.1. Sources

3.1.1. Primary Source(s)

The primary sources of FHC contamination in the Building 637 area release, the ASTs and associated underground piping, appear to have been located and removed through excavation. It is possible that there are other potential FHC sources that exist in the area that could co-mingle with the Building 637 plume. These include abandoned fuel lines between Building 626, the Building 634 gasoline tank, and undocumented fuel spillage within the consolidated motor pool area. Oil and water separators associated with Buildings 638 and 640 have been removed in 1993 and 1996, respectively. However, aside from sporadic detections of chlorinated hydrocarbons in some Building 637 area wells, there is no direct evidence of significant co-mingling.

3.1.2. Secondary Source(s)

Excavation and removal of contaminated soils as an interim remedial action in 1995 probably removed the majority of residual source materials in the Building 637 area. Residual free product has been noted in monitor well W-637-28. From September 1994 to May 1995, an immiscible-phase product skimmer was placed in a newly installed extraction well, 637-EW2, to remove some of the free product. In 1996, monitor well W-637-28 was abandoned during the excavation and removal of about 1,200 cubic yards of soil on the east side of Building 640. During this excavation, soil was excavated from the ground surface to the water table. Areas where free product or a sheen was noted were the primary targets of the excavation and it is possible that all the free product has been removed. Clean sandy material was used to backfill the excavation. Some unknown quantity of residual product may remain trapped in soil pores at or near the water table, and may have the potential to slowly dissolve into groundwater.

3.2. Exposure Pathways

To pose a human health or ecological risk, the source of contaminants (e.g., residual product) must be linked to receptors (e.g., water-supply wells) via pathways. In the case of the Building 637 area, the primary exposure pathway of concern is the potential transport of the dissolved FHC plume through advective, dispersive, and diffusive mechanisms. Biodegradation and retardation processes tend to limit the migration of dissolved hydrocarbons; the input of dissolved FHCs from residual sources is balanced by FHC adsorption onto organic material in the subsurface and FHC loss through biodegradation, integrated over the extent of the plume (McNab et al., 1997). 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). A dissolved plume with limited length reduces the likelihood that receptors may be exposed through the groundwater pathway. Thus, assessing the risk associated with the groundwater pathway at the Building 637 area is directly linked with determining the extent to which biodegradation and retardation are limiting plume migration.

3.2.1. Factors Influencing Groundwater Hydrocarbon Plume

3.2.1.1. Biodegradation

A large body of literature now exists with regard to the biodegradation of BTEX components in groundwater under a variety of environmental conditions. The biodegradation of non-BTEX hydrocarbons (alkanes, alkenes) is less-well characterized, primarily because the toxicologies of these compounds are not as well studied and therefore do not have established maximum contaminant levels (MCLs) for the protection of human health through ingestion. However, biodegradation of these compounds at the Building 637 site is of primary interest because BTEX constituents represent only a very minor component of the groundwater hydrocarbon plume. Nevertheless, studies have indeed shown that non-BTEX components of gasoline and diesel (e.g., *n*- and *i*-alkanes) can undergo biodegradation under ambient conditions (Cozzarelli et al., 1994; Hess et al., 1996; Margesin and Schinner, 1997).

Three lines of evidence exist which suggest that fuel hydrocarbons in groundwater at the Building 637 area are undergoing biodegradation. The first concerns the lower-than-expected concentrations of BTEX components measured in monitor wells. Based on experience at other LUFT sites, BTEX concentrations appear to be substantially depleted compared to other TPHs in the Building 637 area groundwater. Given that BTEX components are more soluble and have a tendency to adsorb onto soils less than other FHCs, this cannot be explained solely by suggesting that the high organic-carbon sediments are retarding the mobility of BTEX compounds. These unexpectedly low concentrations may also be a result of evaporation of BTEX at the surface following release from the above ground storage tanks and prior to infiltration into the subsurface. This may have happened to some minor degree, but given that the BTEX constituents are among the more readily biodegradable of the FHCs, biodegradation offers a more likely explanation.

A second line of evidence pertains to apparent changes in plume geometry over time. Previous studies have shown that hydrocarbon plumes which are undergoing biodegradation tend to show the greatest decline in concentrations in the interior of the plume, with more stable conditions prevailing on the plume peripheries prior to overall plume collapse (Rice et al., 1995; B. Dooher personal communication, 1997). Some wells in the Building 637 area with adequate time series data appear to follow this trend with respect to gasoline range hydrocarbon concentrations.

Finally, geochemical indicator data are generally consistent with expected patterns associated with biodegradation, although the background anaerobic environment may be responsible for muting the signature patterns. A more detailed discussion of the evidence supporting biodegradation of fuel hydrocarbons in Building 637 groundwater is presented in Appendix B.

3.2.1.2. Probability of Plume Stabilization

In principle, a FHC plume may attain a steady-state condition when biodegradation processes remove contaminant mass from solution at a rate equivalent to the influx of fresh contaminant material from dissolution of residual secondary sources. Probabilistic solute transport modeling, based on a conservative transport model and reasonable ranges of values for site parameters, can be used to demonstrate, with high probability, that the dissolved hydrocarbon plume at the Building 637 area is stable. The details of the modeling procedure and findings are presented in Appendix C. In summary, modeling results suggest that substantial further migration of the plume is probable only if the plume is in early stages of formation (i.e., a recent release), if little retardation is occurring, and biodegradation is not significant. Site history, the high organic carbon content of sediments in the area, and the evidence supporting biodegradation (Appendix B) generally indicate that the TPH plume is in a mature, stable stage.

3.2.1.3. Vertical Migration of Contaminants

Vertical migration of contaminants into the underlying B zone aquifer constitutes an additional groundwater migration pathway. However, given (1) the apparent hydraulic isolation of Zone B from the overlying A1 and A2 zones, (2) the lack of observed FHC impact in the B zone, and (3) observed artesian conditions in some B zone wells (suggesting a vertical hydraulic gradient which is upward and not likely to permit downward transport of FHCs) this pathway is considered unlikely.

3.2.1.4. Plume Migration to Surface Waters

Due to minimal tidal influences and infiltration/recharge which is expected to occur in the vicinity of the constructed wetlands, it appears unlikely that petroleum hydrocarbons will be discharged to surface waters (Montgomery Watson, 1995b). Though it appears unlikely, it is important to prevent discharge of petroleum hydrocarbons to the bay or wetlands above concentrations which might cause ecological impacts as discussed in Section 3.3.2.

3.2.2. Hydrocarbon Vapor Migration

Groundwater monitoring data suggest that the FHC plume underlying the Building 637 area has been substantially depleted in volatile aromatic components (i.e., BTEX). Asphalt pavement overlying much of the area provides further protection against hydrocarbon vapor migration. No buildings are planned over the dissolved petroleum hydrocarbon plume.

3.3. Receptors

3.3.1. Present and Anticipated Future Human Health Receptors

No existing human risk receptors for the groundwater (i.e., water supply) or vapor pathway exist in the Building 637 area or downgradient. Beneficial use of the groundwater as a drinking water supply in the immediate area is unlikely due to the high dissolved total solids content of the water reflecting the marine influence.

Individuals engaged in surface activities are not expected to be at risk for inhalation of vapors, since the groundwater monitoring data indicates that the FHC plume underlying the Building 637 area has been substantially depleted in volatile aromatic compounds that could potentially result in a vapor exposure.

Exposure scenarios to workers involved in future wetland restoration efforts in the Crissy Field area could involve dermal contact, ingestion, or possibly inhalation. The probability of such exposure depends on whether or not the FHC plume will move to the area of the proposed wetlands during construction (see Section 3.3.2, below).

3.3.2. Ecological Risk Receptors

The planned construction of a wetlands to the northeast of the site (approximately 550 ft east of the site and about 300 ft south of the leading edge of the plume) is the potential receptor of greatest concern. Under order from the California RWQCB, the Army and its contractor, IT Corporation, undertook a bioassay study designed to determine point-of-compliance concentrations (POCCs) of fuel hydrocarbons in the designated Saltwater Ecological Protection Zone. The procedures and results of this study are presented in IT Corporation (1997).

POCC values of 11.6 mg/kg and 144 mg/kg in wetlands sediments were estimated for gasoline and fuel oil/diesel hydrocarbon ranges. According to the bioassay report,

> "These (concentrations) are considered to be both conservative and protective of both benthic and aquatic species which may inhabit the future wetland areas."

Soil/water partitioning coefficients of 2.5 and 12.1 for the gasoline and fuel oil/diesel ranges (IT Corporation, 1997) suggest that the threshold aqueous concentrations of concern would be approximately 4.6 mg/L and 11.9 mg/L, respectively. Thus, fuel hydrocarbon concentrations in groundwater reaching the wetlands would have to exceed these levels before any measurable adverse ecological impacts would be expected. Current maximum TPH-g concentrations observed in the existing plume are below these concentrations of concern. Further, the plume appears to be stable, given current hydraulic conditions at the Site. While no de-watering is currently planned during wetlands construction, monitoring will need to be conducted during the wetlands construction to verify that the plume is not being affected. Monitoring may also need to be continued after the wetlands construction to determine the extent to which the new wetlands may create a groundwater discharge or recharge area.

3.4. Remedial Goals

Cleanup requirements or standards are set by states to ensure that sufficient contamination is removed to protect human health and the environment. Under this broad umbrella of concerns, state-specific considerations such as groundwater use, aquifer beneficial use designation, cleanup costs versus risks, technical feasibility of cleanup, available expertise, available funding, permitting, land use, and property transfers may also play a role in setting the these standards.

The cleanup standards set by states usually fall into one of three broad categories:

1. Technology based standards, which are based on the detection limits of analytical laboratory equipment.
2. Subjective standards, which are often adopted based on technology limits or in the absence of another mechanism; these standards may require cleanup to a generic level, or non-detectable or background levels.
3. Risk-based standards, which can be either an overall standard based on conservative yet realistic exposure and toxicity analysis, or site-specific standards based on site-specific conditions, land use, and exposure scenarios.

To establish remedial goals, these standards are then applied either at all locations throughout the plume or at some boundary beyond which the plume cannot be allowed to migrate. Remedial goals may also include some time frame within which the goals must be met. The time frame to reach goals can be arbitrary or developed based on the anticipated time until the groundwater resource will probably be used. Important factors to consider in determining an appropriate time frame include: potential for receptor impacts, current water use, historical and future water use projections, land use controls, and plume behavior and control. There are situations in which groundwater may have no probable beneficial use, thus extended timeframes for cleanup are acceptable. The amount and degree of uncertainty in these factors also plays an important role and must be understood and weighed against anticipated costs of cleanup and value of the resource to the public. If conditions at the site do not exceed remedial goals, or can be shown to be naturally progressing to reach these goals within an acceptable time frame, the site will usually receive a status of "no further action required at this time." If, however, site conditions do exceed remedial goals, then several choices exist (Small, 1993):

> Cleanup to background or non-detect: This approach is very protective of human health and the environment, but can often prove to be prohibitively expensive or technically infeasible.
>
> Cleanup to an overall or generic standard: This approach is also usually protective, feasible in many cases, and generally less expensive than cleanup to background or non-detect levels. However, these levels may still prove to be prohibitively expensive, or even technically infeasible for some sites.
>
> Cleanup to a site-specific standard: The protectiveness of this approach is usually based on specified land uses and may need to be re-evaluated if changes occur. The cleanup levels are often more feasible and generally less expensive to achieve. However, this approach requires potentially expensive site-specific exposure and risk assessment, to determine threats and impacts.
>
> Risk management, or containment: When contaminant concentrations exceed safe levels, but cannot feasibly be cleaned up, or there are no current or future exposure pathways, then risk management through containment of contamination to prevent further migration may be an option. Active containment systems are often expensive to install and maintain.
>
> No Action: In some instances, monitoring may not be needed or may eventually be discontinued. This approach may require site-specific exposure and risk assessment, to determine threats and impacts to public health and the environment.

A key consideration in evaluating potential remedial goals are the efforts to transform the Presidio into one of the gems in the national park system. The conversion from a military post to a national park is meant to serve as a model of environmental cleanup. Public stakeholders have argued that because the site is to be used as a national park, land use restrictions are inappropriate, and higher levels of cleanup maybe needed.

It is important to understand that there are technical feasibility limits to removing residual weathered petroleum hydrocarbons and much of what can be done has already been accomplished through extensive over-excavation at the Site. Weathered petroleum hydrocarbons are typically depleted in volatile aromatic components, and the remaining compounds are long-chain hydrocarbons. These long-chain hydrocarbons are relatively insoluble, and immobile compared to the fresh petroleum hydrocarbon volatile aromatic components such as benzene, toluene, or xylenes. For these reasons, it is difficult to extract long-chain hydrocarbons from the subsurface without costly and disruptive actively engineered techniques such as steam flooding or open pit mining.

Fortunately, these long-chain hydrocarbons have much lower toxicity than the volatile aromatic components, ad they naturally degrade through microbial digestion ad geochemical oxidation. This process is usually slower than the biodegradation of the volatile aromatic petroleum hydrocarbon components and the long-chain hydrocarbons may persist for many decades. The Building 637 site appears to already be depleted in volatile aromatic components.

As part of the plume stability analysis, a rough bounding of the time for natural TPH-g plume dissipation was made (Appendix C). The key variable is the volume of the residual hydrocarbons that remain trapped in the subsurface near the release area. An upper bound of greater than one hundred years may be realistic if several thousand gallons remains. This is unlikely since excavation of a majority of the residual hydrocarbons in the area and free-product skimming have resulted in significant reductions in the remaining residual petroleum hydrocarbons. A more likely estimate that assumes only 250 gallons of residual TPH-g remains indicates that several decades may be needed to completely degrade the remaining weathered petroleum hydrocarbons

3.4.1. Remedial Technology or Process Selection

If contaminant concentrations exceed remedial goals and cleanup is required, then a cleanup technology must be selected based on the information obtained from site assessment and characterization. This technology should be selected based on the ability to meet remedial goals, site conditions, and physio-chemical properties of the contaminants. The technology should not create additional hazards (e.g., air sparging without soil vapor extraction that may potentially transport vapors into buildings).

The technology should ideally perform this task as quickly, efficiently, and cost effectively as possible. It is also important to give some consideration to how the cleanup technology or process actually accomplishes concentration reductions and where the removed contaminants or by products are actually going. There are four basic alternatives (Small, 1994):

1. Reuse/recycling.
2. Waste destruction (or conversion).
3. Media transfer.
4. Waste disposal.

Media transfer and disposal options may simply move the contamination to another location where it will have to be cleaned up again. Whereas reuse, recycling, and destruction technologies or processes offer more long-term or permanent solutions.

3.4.2. Remedial Goals and Technology/Process Selection for Building 637 Area

Remedial goals have not currently been clearly established for the Presidio. However, we can match some possible remedial technologies with some possible remedial goals in the following hypothetical examples:

Example (1)

Remedial Goal: Reduce concentrations at all points in the plume to a low value in a short period of time.

Potential Remedial alternative: Excavation of petroleum contaminated soil below the groundwater in the core of the plume and groundwater extraction with above ground treatment for soil and ground water. Monitored natural attenuation at the margins of the plume.

Example (2)

Remedial Goal: Reduce concentrations at all points in the plume to a low value in a longer period of time.

Potential Remedial Alternative: Enhanced and or engineered solutions to accelerate biodegradation in the core of the plume and ground water extraction with above ground treatment for groundwater. Monitored natural attenuation at the margins of the plume.

Example (3)

Remedial Goal: Non-migration or containment of the plume with no surface water impacts allowed.

> Potential Remedial Alternative: Passive bioremediation and monitored natural attenuation for the entire plume. Contingency plan for more active remediation should the plume migrate beyond allowable limits or be mobilized during wetlands construction.

Monitored natural attenuation or passive bioremediation may provide cost-effective containment at some sites. In some instances where contamination exceeds remedial goals, but no immediate threats or impacts are identified, it may be acceptable to allow contamination to remain in place without active remediation. Monitored natural dilution, attenuation, and degradation processes are allowed to slowly reduce concentration levels. However, this approach may require site-specific exposure and risk assessment to determine threats and impacts to public health and the environment (Small, 1993).

4. Summary and Recommendations

Sources. ASTs and associated underground piping have been removed; contaminated soil was removed during subsequent source reduction activities. Any additional limited contributions of FHC contaminants into groundwater would occur through slow diffusive processes operating over a limited extent near the source area.

Pathways. More than one line of evidence suggests that biodegradation processes are active at the site, especially with regard to BTEX constituents. Given this, and the high organic carbon content in the sediments which results in retardation of contaminant movement, the hydrocarbon plume is not expected to undergo further substantial migration.

Receptors. No present or likely future human receptors appear to be at risk of significant exposure to hydrocarbons at the Building 637 area. Bioassay studies suggest that the potential for hazardous exposure of ecological receptors is low. Ecological receptors in the planned Crissy Field wetlands area could be at risk to exposure if groundwater discharge occurs due to wetland construction or operations.

Remediation Options Remedial Options must be selected on the basis of their potential to meet remedial goals. If non-migration (Example 3) is chosen as the remedial goal for this Site, it is our opinion that the risk associated with a natural attenuation remedial option for the dissolved FHC plume at the Building 637 area is low. Human receptors are not threatened. Ecological receptors are unlikely to be impacted because of probable stability of the hydrocarbon plume resulting from biodegradation and the high threshold risk concentrations. It is also our opinion that, regardless of the remedial goal chosen for the Site, natural attenuation and biodegradation will be useful as a component of the overall remedial approach.

A key component for setting remedial goals for this Site includes stakeholder involvement. Stakeholders must feel comfortable that the assumptions associated with the application of the selected remedial option will meet remedial goals within an acceptable period of time. These assumptions must then be validated with performance data from monitoring at the Site as remediation progresses.

To assure adequate protection and verification of assumptions, we recommend a continued monitoring strategy as a safeguard measure. This would include annual sampling of the 14 monitor wells analyzed during the January and April 1997 sampling events. This sampling effort could be modified or discontinued in the future if significant declines in concentration are noted in the majority of the downgradient wells over a period of several years. In the event the concentrations in a number of these wells should exhibit significant increases over time consistent with plume movement, contingency measures, such as an active remediation or hydraulic control strategy, should then be taken into consideration.

5. References

Cozzarelli, I. M., M. J. Baedecker, R. P. Eganhouse, and D. F. Goerlitz (1994), "The geochemical evolution of low-molecular-weight organic acids derived from the degradation of petroleum contaminants in groundwater," *Geochemica et Cosmochimica Acta*, **58**, 863–877.

Hess, A., P. Höhener, D. Hunkeler, and J. Zeyer (1996), "Bioremediation of a diesel fuel contaminated aquifer: Simulation studies in laboratory aquifer columns," *Journal of Contaminant Hydrology*, **23**, 329–345.

IT Corporation (1997), *Report of Petroleum Hydrocarbon Bioassay and Point of Compliance Concentration Determinations, Saltwater Ecological Protection Zone, Presidio of San Francisco, California*, Revision C, p. 49.

Margesin, R., and F. Schinner (1997), "Efficiency of indigenous and inoculated cold-adapted soil microorganisms for biodegradation of diesel oil in alpine soils," *Applied and Environmental Microbiology*, **63**(7), 2660–2664.

McNab, W. W., Jr. (1997), *Statistical Approaches for Assessing Geochemical Signatures of Fuel Hydrocarbon Biodegradation in Groundwater*, Lawrence Livermore National Laboratory, Livermore, Calif. (UCRL-JC-128209).

McNab, W. W., Jr., B. P. Dooher, and J. P. Ziagos (1997), *Evolution of Groundwater Hydrocarbon Plumes: A Comparison of Probabilistic Modeling with Statistical Analyses of Field Data*, Lawrence Livermore National Laboratory, Livermore, Calif. (UCRL-JC-126944).

Montgomery Watson (1995a), *Presidio of San Francisco, San Francisco, California, Building 637 Site Investigation, Final Additional Site Investigation Report.*

Montgomery Watson (1995b), *Presidio of San Francisco, San Francisco, California, Building 637 Area Draft Final Corrective Action Plan.*

Montgomery Watson (1996), *Building 600s Area Site-Specific Groundwater Monitoring Plan, Draft Base Wide Groundwater Monitoring Plan, Presidio of San Francisco, Calif.*

Rice, D. W., R. D. Grose, J. C. Michaelson, B. P. Dooher, D. H. MacQueen, S. J. Cullen, W. E. Kastenberg, L. E. Everett, and M. A. Marino (1995), *California Leaking Underground Fuel Tank (LUFT) Historical Case Analyses*, Lawrence Livermore National Laboratory, Livermore, Calif. (UCRL-AR-122207).

Small, M. C. (1993), "Ex-Situ Corrective Action Technologies," in *Proceedings of the 5th Annual UST/LUST Conference*, San Antonio, Texas, March 22, 1993.

Small, M. C. (1994), "Innovative LUST Cleanup Technologies: Overcoming the Barriers," in *Proceedings of the 4th West Coast Conference on Contaminated Soils and Groundwater*, Long Beach, Calif. (Lewis Publishers).

Williams, P. B., and M. Josselyn (1996), *A Preliminary Design Plan for a 20 Acre Tidal Marsh and Shoreline Restoration at Crissy Fields*, Philip Williams & Associates, Ltd.

Appendix A

Draft Site Assessment Evaluation Letter

Letter Report

Lawrence Livermore National Laboratory

SITE ASSESSMENT REVIEW TO APPLY RISK BASED CORRECTIVE ACTION AT PRESIDIO AT SAN FRANCISCO, BUILDING 637 AREA

The Department of Defense (DoD) Petroleum Hydrocarbon Cleanup Demonstration Program (PHCDP) Expert Committee has reviewed the methods and findings of the site investigations conducted at Presidio of San Francisco, Building 637 area petroleum hydrocarbon release. This letter report is our assessment of the adequacy of the site characterization and site conceptual model as a basis for applying risk-based corrective action (RBCA) methodologies and selecting an appropriate risk management strategy at the Site.

This letter represents the first of two deliverable documents as part of our overall assessment of the Site. It is intended solely as a review of the existing Site data and risk characterization results. Recommendations regarding additional data needed to complete our assessment and refine the Site conceptual model are provided.

A second deliverable will provide site-specific risk management recommendations. Included in the risk management recommendations will be a detailed analysis of key RBCA assumptions and an assessment of site-specific remedial options including the potential biodegradation of petroleum hydrocarbons.

SITE CONCEPTUAL MODEL

A well defined conceptual model of a site contains sufficient information to: a) identify the sources of contamination, b) identify the contaminant fate and transport characteristics of the site, c) determine the nature and extent of the contamination, d) specify potential exposure pathways, and e) identify potential receptors that may be impacted by the contamination.

The Building 637 petroleum release area is part of the Presidio of San Francisco Building 600s area investigation located on Crissy Field. The B-637 area is about 700 feet south of the San Francisco Bay. The B-637 Area has been included in several site investigations since 1990 (Globe Soil Engineering, 1990; Dames & Moore, 1995; Dames & Moore, 1996; Montgomery Watson, 1996). Investigations at the Site include a preliminary site assessment (1989), soil investigation (1990), remedial investigation (1990), site characterization study (1992), and additional site characterization (1993-1994) including an aquifer test (1994) and quarterly groundwater monitoring (1994-1996).

Sources

The B-637 area was formerly a gas station for the Presidio Motor Pool. The gas station was closed and the six above ground tanks and local piping removed in 1989 as a result of damage caused during the Loma Prieta earthquake. The tanks consisted of 3 gasoline and 3 diesel tanks. The volume of the release is unknown. Cone-penetrometer/HydroPunch sampling has been conducted in the area to define the extent of any free product and guide the placement of monitor wells. Storm drain sediment sampling has also been conducted.

The primary sources of petroleum hydrocarbon contamination in the B-637 area release appear to have been located and removed through over-excavation during the initial tank removal action and during later removal actions. Approximately 1000 cubic yards of soil were removed during 1995. Five hundred cubic yards of the excavated soil were treated at the Low Temperature Thermal Desorption (LTTD) unit located near the B-637 site. Imported clean granular material was used to backfill the Site. During 1996, an additional over-excavation of more than 1,000 cubic yards of material was performed down to the water table, east of B-640, to remove any residual petroleum contaminated soil. Originally, about one foot of gasoline free product was observed at the Site. A pump and treat system, including a free product skimmer, operated for nine months during 1994-1995, and approximately 70-90 gallons of free product were recovered.

Fate and Transport Characteristics

The subsurface hydrogeologic setting has been well characterized through more than 50 borings to sample sediments and construct groundwater monitor wells and piezometers. Additionally, a seismic reflection survey (Resolution Resources, Inc., 1995) and a geotechnical investigation (Golder Associates, Inc., 1993) was conducted. As a result, geologic and depositional site conceptual models are well developed.

The groundwater is shallow, approximately three to seven feet below the ground surface, and flows slowly, about 85 to 400 feet per year to the north west, toward the San Francisco Bay. There are three aquifer zones, A1, A2, and B, each separated by a fine grained, organic rich estuarine unit that acts as an aquitard. A deeper C zone that is in contact with bedrock has not been studied in the same detail as the A and B zones, because groundwater samples have showed no apparent petroleum hydrocarbon contamination. Reports indicate a considerably thicker aquitard between the A2 and B zones than the A1 and A2 zones. The B zone appears to be confined and monitor wells completed in this zone were observed to be artesian which may tend to prevent contaminant migration from the A zone to the B zone. It is likely that the artesian conditions within the B zone are the result of density differences between the fresh water in the B zone and the salt water intruding into the zone from the Bay. These conditions will also tend to prevent contaminant migration along the B zone into the San Francisco Bay.

Several wells which were installed in the early stages of the investigation were unknowingly screened across the A1 and A2 aquitard. These wells have been removed and replaced with wells screened in the appropriate zones.

Tidal influence upon groundwater surface elevation is minimal except for within the B zone. Seasonal groundwater surface elevation fluctuations of about two feet have been observed in the A zones. Seasonal ground water surface fluctuations in the B zone have been measured for seven quarters, but have not been analyzed yet.

The Site is located at the base of a serpentinite bedrock hill to the south, and the three aquifer zones abut the regolith at the base of the bedrock. The regolith may communicate with and provide recharge to the deeper aquifer zones.

A key characteristic of the Site that is influencing fate and transport of petroleum hydrocarbons is soil organic carbon. The organic carbon at the Site is very high due to the estuarine nature of the sediments. The high organic carbon in the soil will strongly sorb petroleum hydrocarbon contamination and restrict contaminant movement.

Nature and Extent of Contamination

The contaminants identified in the soil and groundwater at the Site consist of volatile aromatic hydrocarbons, total petroleum hydrocarbons as gasoline (TPHg) and diesel (TPHd). Sampling and analysis was conducted for MTBE during the April, 1996, monitoring event and was not detected in any well at the B-637 site at the reporting limit of 5 µg/l.

As a result the principal compounds of concern are BETX for TPHg and TPHd. In 1995, the hydrocarbon plume, as characterized by TPHg analysis, extended about 640 feet and, as characterized by TPHd analysis, about 400 feet down gradient to the north west in the A1 Zone. In the A2 zone, the TPHg range hydrocarbon plume extended about 160 feet down gradient, and TPHd range hydrocarbons were not detected. Benzene concentrations have been observed to range from 2.8 to 84 µg/l in the A1 zone and from 0.6 to 390 µg/l in the A2 zone.

Benzene is currently believed to be present only in the A zone. Benzene was observed in the B zone only once. During 1994, a sample from well 637-22, indicated benzene below the analytical detection limit and was estimated to be about 0.7 µg/l. Benzene has not been detected in this zone since. The highest diesel range TPH concentration was observed in the upper B Zone. However, these high results were obtained via hydropunch sampling that was directly through free product in the A1 zone. A well (637-17) in the B zone was installed as a result of these initial results. Prior to the initiation of the use of silica gel cleanup during sample analysis, four quarters of sampling were performed. The results of this sampling indicated diesel range organics at about 170 µg/l. A subsequent sampling event that have used the silica gel cleanup during sample analysis did not detected diesel range organics. There is a possibility that the single initial detection of diesel range organics may represent naturally occurring compounds. There is also a possibility that smearing of the free product into the B zone during hydropunch operations may also account for the initial detection of diesel range organics.

Groundwater sampling results during 1996 indicate petroleum hydrocarbon concentrations are decreasing in the A zone. However, there are several issues which remain regarding the distribution of petroleum hydrocarbons observed in the groundwater. The first regards the use of TPH analysis for gasoline and diesel . The use of TPH analytic methods as part of the application of RBCA presents several problems. One is that TPHg and TPHd are non-chemical specific. Compounds which contribute to an exposure risk are not specifically identified during analysis. It is possible to have relatively high TPHg or TPHd measurements and yet have relatively low concentrations of hazardous compounds. Further, there are a variety of naturally occurring organic compounds that show up during the TPHg and TPHd analysis that may be not associated with a petroleum hydrocarbon release. This problem has been recognized by the B-637 site investigators and silica gel sample cleanup (modified USEPA Method 3630A) is currently being used to remove these natural organic compounds from groundwater prior to sample extract analysis. This change in sample extract analysis procedure has raised some questions regarding the extent of the petroleum hydrocarbon contamination. These issues will be further researched and discussed as part of the Expert Committee assessment of the B-637 area plume behavior and site-specific risk management recommendations.

Another issue regarding the distribution of petroleum hydrocarbons, concerns the overall unexpected absence of benzene, toluene, ethyl benzene and xylene constituents in groundwater at the Site. While benzene has been observed sporadically in monitor wells, it is not observed to the degree that might be anticipated, based on observed concentrations of TPH for gasoline and diesel. The ability of the organic carbon rich soil at the Site to sorb petroleum hydrocarbons may account for the unexpectedly low concentrations of benzene observed in the groundwater. There is also a possibility that naturally occurring biodegradation processes are removing the benzene from the groundwater. Additional sampling for inorganic ions in the groundwater indicative of biodegradation may provide insight into the mechanisms contributing to the unexpectedly low observed concentrations of benzene.

The sporadic occurrence of benzene may be associated with rainfall events, or other processes which may release benzene from the unsaturated zone. It may also be possible that there are other potential up-gradient petroleum hydrocarbon sources that could co-mingle with the B-637 plume and these sources are intermittently releasing benzene. Alternatively, groundwater extraction during sampling or excavation may draw benzene from unidentified nearby sources. These potential sources include abandoned fuel lines between B-626 and the B-637 gasoline tank, oil water separators in Buildings 640 and 638 (both removed with little or no benzene contamination), and fuel spillage within the consolidated motor pool area. The Army plans an extensive investigation in and around the historic motor pool area as well as the gasoline lines running to and from the B-637 site to assess the potential for commingling plumes. To date, HydroPunch samples located in the LTTD area, up gradient from the B-637 area, did not show groundwater contamination.

Exposure Pathways

During the 1992 site characterization study a soil gas survey was conducted. Soil vapor survey data have not been provided at this time to evaluate the potential inhalation hazards to receptors.

Although the San Francisco Bay Regional Water Quality Control Board’s Basin Plan designates the ground water at the Site as municipal beneficial use, the anticipated time frame for beneficial use may be very distant or never. The use of the groundwater is improbable because of the proximity of the high total dissolved solids in groundwater adjacent to the bay, ground settlement concerns if water were to be extracted, and existence of other higher quality aquifers at the Presidio (e.g. Lobos Creek aquifer).

It is important to protect the B zone which is currently believed to have no petroleum hydrocarbon contamination and may communicate with the San Francisco Bay ecosystem. Currently, wells within the A zone which have been screened over more than one layer have been closed and there are no wells screened in the B zone. It appears that recharge through the regolith at the base of the hills near the source area is a potential pathway for contaminant migration to the deeper B zone. Current groundwater data for the site indicate that this has not been the case and the artesian conditions within the B zone will tend to prevent contaminant migration along the B zone into the San Francisco Bay.

Potential Receptors

The proposed future land use of Crissy Field includes construction of a wetland to the northeast of the B-637 area and restoration of the historic airfield directly north and to the west of the Site. In our opinion, the planned construction of a wetlands adjacent to the Site (approximately 400 feet laterally cross gradient to the leading edge of the plume) may increase the probability of B-637 petroleum hydrocarbon contamination impacting wetland ecology. Although the groundwater flow direction is currently away from the proposed wetlands and the probability of petroleum hydrocarbons from the B-637 area reaching the constructed wet lands may be low, the expert committee has not currently been provided with the results of the Army’s hydraulic modeling effort to evaluate this scenario. It is possible that dewatering during wetlands construction could mobilize the petroleum hydrocarbon plume moving it closer to the wetlands. However, it is also possible that recharge during operation of the wetlands could act as a hydraulic barrier to intrusion of the hydrocarbon plume.

Since the groundwater in the Crissy Field area, including B-637 impacted groundwater, has been deemed "low probability of use", the San Francisco Regional Water Quality Control Board (RWQCB) has not been insisting that cleanup to background is appropriate prior to site closure. The RWQCB and the Army have agreed that the existence of a receptor, (e.g., wetland or the bay), nearby does not automatically mean that an exposure will occur. The RWQCB and the Army have also agreed that if modeling shows that a receptor will be impacted then cleanup goals will be based on anticipated risk to that receptor. If modeling shows no impact to receptors, then default groundwater exposure scenario is to a construction worker. Further, the

Army has agreement from the RWQCB that the point of compliance will be where the impact occurs, not the source area.

The potential for inhalation hazards to humans from the B-637 plume is very unlikely since relatively low concentrations of volatile petroleum hydrocarbon compounds have been observed. Soil vapor sampling can be used to confirm that no potential exposure exists.

There do not currently appear to be any impacts to receptors at the site. Potential impacts to the proposed reconstructed wetlands may warrant some further consideration. Thus, cleanup by natural attenuation processes maybe a viable remedial alternative at the Site. A performance standard or performance based remedial goal may also be viable alternatives at the Site.

SUMMARY AND RECOMMENDATIONS

A well defined conceptual model to apply RBCA at the B-637 area should:

a) identify the sources of contamination,
b) identify the contaminant fate and transport characteristics of the site,
c) determine the nature and extent of the contamination,
d) specify potential exposure pathways, and
e) identify potential receptors that may be impacted by the contamination.

Sources: Sufficient data have been collected to define the source of contamination resulting from the B-637 leak and the source area has been removed. Other sources may have contributed to the groundwater petroleum hydrocarbon contamination in the areas adjacent to B-637 and there is a possibility of co-mingled groundwater plumes.

Site contaminant fate and transport characteristics: While benzene has been observed sporadically in monitor wells, it is not observed to the degree that might be anticipated, based on observed concentrations of TPH for gasoline and diesel. The ability of the organic carbon rich soil at the Site to sorb petroleum hydrocarbons may account for the observed low concentrations of benzene in the groundwater. There is also the possibility that naturally occurring biodegradation process are removing the benzene from the groundwater.

The Site hydrogeologic setting is well defined. The current direction and rate of groundwater flow at the Site is well characterized, but there are uncertainties about future hydraulic conditions during construction and operation of the proposed wetlands.

Nature and extent of contamination: The nature of the contamination is well defined and the contaminants of concern are BETX Compounds, TPHg and TPHd. However, there is still some uncertainty regarding the extent of contamination because of the change in sample extraction cleanup procedures.

Pathways: It is important to protect the B zone which is currently believed to have no petroleum hydrocarbon contamination. There is uncertainty regarding the potential for recharge through the regolith at the base of the hills near the B-637 area to potentially carry contaminants to the deeper B zone.

Potential receptors: The general absence of benzene and the low probability of groundwater ingestion or use indicates that the Site may have a low probability of impacting any receptors and that a natural degradation or depletion mechanism maybe operating at the Site that will restrict hydrocarbon movement. Further evaluation of potential vapor impacts is needed. There is currently not enough information to evaluate potential impacts to the proposed constructed wetlands.

To assist the Army in refining the B-637 Site conceptual model and address areas of uncertainty the Expert Committee makes the following recommendations and requests for additional data:

Sources: The Expert Committee recommends that available rainfall data be correlated with the sporadic occurrence of benzene to help evaluate the hypothesis that the absence of benzene may be related to the sorption of petroleum hydrocarbons on the organic rich soil at the Site. The Expert Committee also request the results of any on-going investigations in and around the historic motor pool area and gasoline lines running to and from the B-637 site.

Site fate and transport characteristics and exposure pathways: The Expert Committee suggests that additional sampling for inorganic ions in the groundwater indicative of biodegradation may provide insight into the mechanisms contributing to the unexpectedly low observed concentrations of benzene. Such sampling should include electron acceptor concentrations (i.e., dissolved oxygen, nitrate, sulfate, iron, manganese) and other biodegradation indicators (e.g., alkalinity/bicarbonate, methane, Eh, pH). For these data to be useful for assessing biodegradation, samples should be collected from a number of wells, including wells representative of background conditions or cross-gradient conditions away from the plume center.

Nature and extent of contamination: The Expert Committee would like to review the study of the sampling that compared groundwater analytical results with and without silica gel cleanup (Montgomery Watson, 1995e). The current thinking among the Expert Committee members is that Gas Chromatography (GC)/Mass Spectrometry (MS) confirmation may be needed to assure that the silica gel cleanup process is not removing chemicals of concern and giving false negative results. This will be assessed further after the Expert Committee reviews the Army's B zone analysis study and discussed as part of the site-specific risk management recommendations

Pathways: The Expert Committee recommends that the potential for vertical gradients through the regolith at the base of the hill to the south of the B-637 area be evaluated. Data from overall Building 600s area characterization could be used to evaluate vertical gradients through the regolith at the base of the hill.

Potential receptors: The Expert Committee requests additional information on plans for construction or occupation of structures over the B-637 petroleum hydrocarbon plume so the potential inhalation hazards associated with anticipated land use scenarios can be evaluated. Soil vapor data will be useful to evaluate the potential inhalation hazards to receptors using the restored historic airfield. The Expert Committee also requests any available results of the Army's hydraulic modeling effort to evaluate possible changes in hydraulic conditions during construction and operation of the proposed wetlands.

Sincerely,

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DR/MS:cak

Appendix B

Evidence of Biodegradation of Fuel Hydrocarbons in Groundwater at B-637

Appendix B

Evidence of Biodegradation of Fuel Hydrocarbons in Groundwater at B-637

B-1. Patterns of Plume Collapse

Recent statistical analyses of the historical behavior of hydrocarbon plumes indicates that as plumes begin to attenuate through biodegradation processes, the higher concentrations in the plume interior tend to decline most rapidly, with concentrations on the plume margins remaining relatively stable (Rice et al., 1995; B. Dooher, personal communication, 1997). To identify trends in the B-637 area, gasoline-range hydrocarbon concentrations were assessed as a function of time in monitoring wells where a sufficient number of detections has occurred since July 1995 (following initiation of the silica gel cleanup processes) to permit correlation analyses. Two non-parametric (rank-based) correlation methods, Spearman's correlation coefficient and Kendall's τ, were employed as opposed to normal linear regression to offset the effects of possible outliers. The results of the correlation analyses are shown on Table B-1. With the exception of 637-32, concentrations in the wells which were evaluated either declined (637-01R, 637-26, 637-27, LF07GW11) or exhibited no clear trend (637-25). The apparent increase in 637-25, a monitoring well located on the current periphery of the plume, may not be statistically significant. The temporal variations in concentration in three of these wells are shown on Figure B-1.

Table B-1. Correlation coefficients pertaining to the relationship between gasoline range hydrocarbon concentrations and time.

Well	Average conc. over time (ppb)	Spearman's R	Kendall's τ
637-01R	**871**	**-0.541**	**-0.488**
637-25	**1,655**	**-0.029**	**0.000**
637-26	**1,750**	**-1.000**	**-1.000**
637-27	**490**	**-0.771**	**-0.600**
637-32	**135**	**0.429**	**0.333**
LF07GW11	**182**	**-0.829**	**-0.733**

Although this analysis of time series data does not prove plume stability, the findings are not inconsistent with those of typical plumes undergoing biodegradation as observed in the LUFT Historical Cases Analysis (Rice et al., 1995). Moreover, there does not appear to be any significant evidence of substantial plume migration during the 1995–1997 time period.

B-2. Geochemical Indicators of Biodegradation

Secondary evidence often consists of an assessment of changes in groundwater geochemistry associated with the FHC plume which may reflect the oxidation of FHCs by microorganisms (e.g., Vroblesky and Chapelle, 1994; Borden et al., 1995). For example, idealized mineralization reactions of toluene, a common soluble and degradable FHC constituent, to yield carbon dioxide may include:

$$C_7H_8 + 9O_2 \rightarrow 7CO_2 + 4H_2O \qquad \text{(C-1)}$$

$$C_7H_8 + 18MnO_2 + 36H^+ \rightarrow 7CO_2 + 18Mn^{2+} + 22H_2O \qquad \text{(C-2)}$$

$$5C_7H_8 + 36NO_3^- + 36H^+ \rightarrow 35CO_2 + 18N_2(g) + 38H_2O \qquad \text{(C-3)}$$

$$C_7H_8 + 36Fe(OH)_3 + 72H^+ \rightarrow 7CO_2 + 36Fe^{2+} + 94H_2O \qquad \text{(C-4)}$$

$$2C_7H_8 + 9SO_4^{2-} + 18H^+ \rightarrow 14CO_2 + 9H_2S + 8H_2O \qquad \text{(C-5)}$$

$$2C_7H_8 + 10H_2O \rightarrow 14CO_2 + 9CH_4 \qquad \text{(C-6)}$$

Laboratory studies have confirmed FHC biodegradation reactions by specific electron acceptors (e.g., Lovley et al., 1989; Beller et al., 1992; Lovley et al., 1995; Vroblesky et al., 1996). Thus, solution constituents which may serve as biodegradation indicators include electron acceptors (dissolved oxygen, nitrate, sulfate), reduced by-products of FHC oxidation reactions (ferrous iron, manganese, methane), solution redox potential or E_h, and indicators of mineralization (bicarbonate alkalinity, pH via dissociation of carbonic acid). Sulfide, also a reduced by-product of FHC biodegradation, is often not measurable because of the low solubility of sulfide-bearing minerals under typical E_h-pH conditions.

Geochemical indicator data have been collected from 14 groundwater monitoring wells in the B-637 area in both January 1997 and April 1997 sampling rounds. Data analyses techniques have been developed as part of the Department of Defense Petroleum Hydrocarbons Demonstration Program to evaluate geochemical indicator signatures in FHC-contaminated aquifers (McNab, 1997). These include correlation analyses to assess trends in geochemical parameter values in relation to hydrocarbon concentrations as well as population means hypothesis testing to identify statistically significant differences in geochemical parameter values between FHC-contaminated and uncontaminated water samples.

The results of correlation analyses between gasoline range hydrocarbon concentrations and geochemical indicator parameter values in 1997 groundwater sampling data are shown on Table B-2. Two types of correlation analyses were performed. These consist of Pearson's correlation coefficient, the familiar correlation coefficient yielded by a normal linear regression (with the hydrocarbon concentration as the independent variable), as well as Spearman's rank-based correlation coefficient to minimize the effects of outliers. Correlation coefficients yielded by Spearman's method suggest that manganese and iron concentrations provide some evidence of biodegradation, reflecting manganese and iron reduction and mobilization processes (i.e., Eqs. C-2 and C-4). Bicarbonate concentrations, which would be expected to indicate hydrocarbon mineralization, show a weak positive trend with respect to hydrocarbon concentrations. Redox potential, which has been shown to usually exhibit strong negative correlations with BTEX concentrations at other sites (McNab, 1997), exhibits a very weak negative correlation at the B-637 site. The remaining geochemical indicators show trends that are even weaker, or, in the case of sulfate, inconsistent with expectation (i.e., a positive trend with hydrocarbon concentrations instead of a negative trend). Pearson's correlation method generally produced poor results.

Chloride, which does not participate in biodegradation reactions, is included as a control in the correlation analyses.

Table B-2. Correlation coefficients pertaining to the relationship between geochemical bioattenuation indicators and gasoline range hydrocarbon concentrations in 1997 B-637 area groundwater samples.

Parameter	Pearson's R	Spearman's R
Mn^{2+}	0.554	0.616
Fe^{2+}	0.182	0.498
HCO_3^-	-0.058	0.386
E_h	-0.280	-0.238
pH	-0.187	-0.204
CO_2	0.113	0.167
NO_3^-	0.126	-0.127
CH_4	-0.020	0.121
SO_4^{2-}	0.208	0.115
Cl^-	0.271	-0.041
O_2	0.153	0.016

The second method of analysis involves comparing geochemical indicator parameter values between groundwater samples containing detectable gasoline-range hydrocarbons and those which do not. Population means differences tests, such as the familiar student's t-test, are useful for establishing confidence levels as to whether or not the two samples are likely to originate from the same data set. Non-parametric equivalents of the t-test, such as the Mann-Whitney test statistic, are ranked based methods which offer advantages in analyzing data which exhibit large ranges of values.

Median concentrations of geochemical indicator parameter values from the two sample sets, and the corresponding Mann-Whitney test results, are shown on Table B-3. A comparison of the median values of the geochemical indicators shows that all are consistent with a biodegradation hypothesis (i.e., all show qualitative agreement with Eqs. C-1 through C-6), with the exception of dissolved oxygen. In particular, the relatively high levels of methane are consistent with methanogenesis. The Mann-Whitney test results generally support the assertion that the two sample populations (FHC-impacted and unimpacted) are significantly different from one another with respect to the indicator parameters (The Mann-Whitney test result is the probability that the null hypothesis, asserting the two samples are associated with the same data set, is true. Consequently, a low probability for the null hypothesis implies a high probability that the two sample sets are significantly different from one another). However, the Mann-Whitney test result also implies a high level of confidence that chloride concentrations differ significantly between the two sets, which would not be expected based on biodegradation process arguments. It is possible that this is a real effect (i.e., chloride concentrations may be elevated downgradient of the main portion of the plume because of proximity to saline Bay water), or that the Mann-Whitney method is overly sensitive to otherwise meaningless differences in water chemistry. The implication is that while the patterns in geochemical indicator parameters are consistent with biodegradation when grouped into contaminated and uncontaminated wells, the significance of the observed differences must be interpreted with caution.

Table B-3. Median values, and confidence levels in the null hypothesis of significant differences in population means, in geochemical bioattenuation indicators between FHC-impacted and unimpacted groundwater samples.

Parameter	Gasoline- range FHCs below DL (ppb)	Gasoline- range FHCs above DL (ppb)	Mann-Whitney test result
Mn^{2+}	532	1,010	0.00%
HCO_3^-	400,000	519,000	0.01%
CH_4	2,100	7,800	0.08%
CO_2	44,150	54,200	0.14%
Fe^{2+}	117	4,980	0.67%
SO_4^{2-}	36,750	31,700	1.23%
NO_3^-	60	30	1.24%
E_h	-57	-76	2.67%
Cl^-	104,000	93,700	3.27%
pH	6.97	6.83	3.46%
O_2	0.39	0.42	82.60%

In conclusion, it appears that geochemical indicator data support the hypothesis of biodegradation at some level. Low levels of background dissolved oxygen and Eh (refer to Fig. C-2) suggests that the ambient environment in the B-637 area is generally anaerobic, which is to be expected in an environment characterized by significant natural organic material. It is likely, therefore, that the geochemical signatures of biodegradation are less easily identified than in more aerobic environments, hence the relatively weak direct correlations between indicator values and hydrocarbon concentrations. Nevertheless, observations are consistent with a plume geochemical environment largely controlled by iron or manganese reduction and methanogenesis.

Biodegradation of fuel hydrocarbons under similar conditions has been well-documented at a crude oil release site in Bemidji, Minnesota, by the U.S. Geological Survey and others (e.g., Baedecker et al., 1993).

References

Baedecker, M. J., I. M. Cozzarelli, R. P. Eganhouse, D. I. Siegel, and P. C. Bennett (1993), "Crude oil in a shallow sand and gravel aquifer, 3. Biogeochemical reactions and mass balance modeling in anoxic groundwater," *Applied Geochemistry*, **8**(6), 569-586,.

Beller, H. R., D. Grbic-Galic, and M. Reinhard (1992), "Microbial degradation of toluene under sulfate-reducing conditions and the influence of iron on the process," *Applied and Environmental Microbiology*, **58**, 786–793.

Borden, R. C., C. A. Gomez, and M. T. Becker (1995), "Geochemical indicators of intrinsic bioremediation," *Ground Water*, **33**(2), 180–189.

Lovley, D. R., M. J. Baedecker, D. J. Lonergan, I. M. Cozzarelli, E. J. P. Phillips, and D. I. Siegel (1989), "Oxidation of aromatic contaminants coupled to microbial iron reduction," *Nature*, **339**(5), 297–300.

Lovley, D. R., J. D. Coates, J. C. Woodward, and E. J. P. Phillips (1995), "Benzene oxidation coupled to sulfate reduction," *Applied and Environmental Microbiology*, **61**, 953–958.

McNab, W. W., Jr. (1997), *Statistical Approaches for Assessing Geochemical Signatures of Fuel Hydrocarbon Biodegradation in Groundwater*, Lawrence Livermore National Laboratory, Livermore, Calif. (UCRL-JC-128209).

Rice, D. W., R. D. Grose, J. C. Michaelson, B. P. Dooher, D. H. MacQueen, S. J. Cullen, W. E. Kastenberg, L. E. Everett, and M. A. Marino (1995), *California Leaking Underground Fuel Tank (LUFT) Historical Case Analyses*, Lawrence Livermore National Laboratory, Livermore, Calif. (UCRL-AR-122207).

Vroblesky, D. A., and F. H. Chapelle (1994), "Temporal and spatial changes of terminal electron-accepting processes in a petroleum hydrocarbon-contaminated aquifer and the significance for contaminant biodegradation," *Water Resources Research*, **30**(5), 1561–1570.

Vroblesky, D. A., P. M. Bradley, and F. H. (1996), "Chapelle, Influence of electron donor on the minimum sulfate concentration required for sulfate reduction in a petroleum hydrocarbon-contaminated aquifer, *Environmental Science and Technology*, **30**, 1377–1381.

Appendix C

Forecasting Plume Stability

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Forecasting Plume Stability

C-1. Modeling Approach

The LUFT Historical Cases Analysis (Rice et al., 1995) revealed statistical evidence suggesting that dissolved BTEX plumes typically stabilize after reaching a certain length. Benzene plume lengths, for example, ranged from approximately 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 passive bioremediation) integrated across the plume.

Simple analytical solutions to the advective-dispersive solute transport equation may be used to assess plume stability and to forecast the probability of further plume expansion, given certain assumptions concerning boundary conditions and representative transport parameters. Domenico (1987) presented a solution of the form,

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

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

for two-dimensional transport 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, 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 solution assumes uniform, steady flow and a continuous line source which may be thought of as representing a residual lens of NAPL. The geometry corresponding to this plume model is shown on Figure C-1.

At some particular time t, the length of the plume in the downgradient direction (i.e., the distance between the origin and some specified contour interval), L, may be calculated by setting $y = 0$ and solving Equation C-1 for x in an iterative manner using the bisection method or Newton's method. Plume length estimates via Equation C-1 depend on the values of the longitudinal and transverse dispersivities, α_x and α_y, which are used to account for the macrodispersive effects of a flow field exhibiting local-scale variability. Longitudinal dispersivity is commonly assumed to be equivalent to some fraction of the length scale of the plume; typically a value on the order of 0.1 is used. Calculation of dispersivity values and plume lengths can be viewed as an iterative process. As a first approximation, longitudinal dispersivity is assumed to equal a fraction of the length scale of the plume as defined by the groundwater velocity multiplied by elapsed time. This is used to obtain a preliminary estimate of plume length. The longitudinal dispersivity value is then refined according to the new plume length estimate. Transverse dispersivity is assumed to equal a fraction of the longitudinal dispersivity.

The absolute plume growth rate may be calculated by,

$$\frac{dL}{dt} \approx \frac{L_{Q2} - L_{Q1}}{\Delta t} \tag{C-2}$$

where L_{Q1} and L_{Q2} refer to plume lengths over consecutive quarters, and Δt the monitoring period (e.g., one quarter, or approximately 91 days). A normalized plume growth rate, which expressed plume growth rate as a simple percentage in units of time^{-1}, can be calculated by dividing dL/dt by the mean plume length,

$$L_{mean} = \frac{L_{Q2} + L_{Q1}}{2} \tag{C-3}$$

C-2. Plume Stabilization and Probabilistic Modeling

Application of this modeling procedure to a site such as the B-637 area clearly implies a high degree of idealization because a simple analytical solution is not capable of simulating the effects of heterogeneities in the flow field or complex boundary and initial conditions. However, such a modeling approach is useful for illustrating general trends which would be expected in the data, based on simple assumptions concerning the subsurface environment. Inspection of Equation C-1 indicates that values of C_0, Y, λ, v, R, α_x, α_y, and t must be provided to the model in order to generate an estimated plume length. Some of these parameters may be estimated using conservative assumptions (e.g., C_0, λ) or else estimated from site data, as in the case of v, which may be calculated by Darcy's law,

$$\mathrm{v} = \frac{\mathrm{K}\nabla \mathrm{h}}{\phi} \tag{C-4}$$

where K refers to hydraulic conductivity, ∇h the hydraulic gradient, and ϕ the sediment porosity.

Probability distributions for the pertinent parameters, and the rationale for the proposed distributions, are listed on Table C-1. A simple example of plume stabilization can be demonstrated by calculating plume length as a function of time, using the procedure outlined above, for representative values of model parameters selected from these distributions. Results of this type of calculation using the representative values given on Table C-1 are shown on Figure C-2. Using these values and the assumptions and procedures presented above, the model predicts that the gasoline range hydrocarbon plume, as defined by the 10 ppb contour, should stabilize at approximately 620 feet after 10 years elapsed time. This is roughly consistent with present observation. Nevertheless, the considerable uncertainty associated with each of the model parameters implies that a broader range of plume evolution histories must be considered and parameter sensitivities evaluated.

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

Parameter	Units	Distribution	Typical representative value (for demonstration only)	Basis
C_0, source concentration	mg/L	Normal. 100 ± 10.	50	Based on typical observed maximum aqueous concentrations of gasoline (assuming contact with NAPL).
Y, source width	ft	Lognormal. 10% = 10; 90% = 100.	30	Postulated.
λ, decay coefficient	day^{-1}	Lognormal. 10% = 0.05%; 90% = 0.50%.	0.20%	Postulated, based on reported values for mean first-order degradation constants at other LUFT sites (e.g., MacIntyre et al., 1993; Wilson et al., 1995; Buscheck et al., 1996; Chapelle et al., 1996); adjusted downward to address non-BTEX constituents under strictly anaerobic conditions (see Appendix B).
K, hydraulic conductivity	ft/day	Lognormal. 10% = 27; 90% = 45.	36	Based on site data.,
∇h, hydraulic gradient	–	Lognormal. 10%=0.002; 90%=0.006.	0.004	Based on site data.
ϕ, porosity	–	Lognormal. 0.25 ± 0.03.	0.25	Postulated.
R, retardation coefficient		Lognormal. 10% = 2; 90% = 20.	5	Postulated.

Table C-1. (Continued)

Parameter	Units	Distribution	Typical representative value (for demonstration only)	Basis
α_x ratio (ratio of longitudinal dispersivity to plume length scale, *vt*).	**–**	**Lognormal. 10% = 0.03; 90% = 0.33 (median = 0.10).**	**0.1**	**Postulated (based on the standard assumption that α_x ~ 10% plume length).**
α_y ratio (ratio of transverse dispersivity to longitudinal dispersivity).	**–**	**Lognormal. 10% = 0.03; 90% = 0.33 (median = 0.10).**	**0.1**	**Postulated (based on the standard assumption that α_y ~ 10% x α_x).**
t, time elapsed between introduction of source and groundwater quality sample	**years**	**Lognormal. 10% = 5; 90% = 50.**	**–**	**Postulated; based on history of ASTs.**

Monte Carlo analyses offer a means by which probabilistic forecasts of plume length may be developed. This approach involves generating random sets of model parameters from the prescribed probability distribution functions and conducting multiple simulations, or realizations, each with an individual plume length (and growth rate). The resulting assemblage of lengths and growth rates may be used to construct probability distribution functions. Sensitivity analyses may then be performed which quantify the correlation between variance in forecast values and uncertainties in model parameters.

The forecast probability distribution of plume lengths for 2,000 Monte Carlo realizations is shown on Figure C-3. The median forecast length, approximately 560 ft, is reasonably consistent with the observed extent spatial extent of the present plume. The corresponding forecast probability distribution of plume growth rates is shown on Figure C-4. The median forecast rate of growth is approximately 3×10^{-6} day^{-1} (essentially stable).

Sensitivity analyses were performed using a rank correlation method (Kendall's τ) to develop correlation coefficients between forecast lengths and growth rates and model parameter values. The resulting correlation coefficients are given on Table C-2.

Table C-2. Correlation coefficients relating model forecasts to parameter values, as determined by Kendall's τ.

Parameter	Plume length	Plume growth rate
C_0, source concentration	0.015	-0.003
Y, source width	0.063	0.037
λ, decay coefficient	-0.350	-0.433
K, hydraulic conductivity	0.077	-0.021
∇h, hydraulic gradient	0.220	-0.017
ϕ, porosity	-0.037	-0.004
R, retardation coefficient	-0.449	-0.016
α_x ratio (ratio of longitudinal dispersivity to plume length scale, *vt*).	0.222	-0.050
α_y ratio (ratio of transverse dispersivity to longitudinal dispersivity).	-0.019	0.005
t, time elapsed between introduction of source and groundwater quality sample	0.150	-0.458

The sensitivity analyses suggest that variance in forecast plume lengths most strongly reflects uncertainty in the first-order decay coefficient as well as the retardation coefficient, whereas variance in plume growth rate primarily reflects the age of the plume and the decay coefficient. The relationships between plume length, growth rate, elapsed time, and decay rate are further illustrated on Figure C-5 and Table C-3.

Table C-3. Median forecast plume lengths and growth rates over intervals of elapsed time since source initiation.

Elapsed time (years)	Plume length (ft)	Plume growth rate (day^{-1})
<5	332	5.0×10^{-4}
5-25	552	1.9×10^{-5}
>25	614	6.0×10^{-9}

In summary, probabilistic modeling results suggest that the likelihood of significant further expansion of the hydrocarbon plume at the B-637 site is probably very low, even given all of the uncertainties in model parameters. The only scenario by which significant further plume growth could be expected would involve a very young plume subject to little retardation or passive bioremediation. The site history, the high organic carbon content of subsurface sediments, and independent evidence supporting passive bioremediation imply that this scenario is not likely. Furthermore, the model results are conservative in that a constant source concentration is assumed.

In reality, this would be expected to diminish substantially over time following remedial action, such as contaminated soil excavation, as well as secondary residual pestroleum hydrocarbon depletion resulting from dissolution and volatilization.

C-3. Constraints On Plume Dissipation

The Domenico (1987) solution to the solute transport equation assumes a constant concentration boundary condition, which is a highly conservative assumption, given that contaminant sources will decline through time as the NAPL becomes depleted due to dissolution, volatilization, and other mechanisms (including engineered source removal and excavation). An alternative solution to the Domenico (1987) model is that of Cleary and Ungs (1978), which uses the same assumptions but also includes a source attenuation term, β, which is a first-order decay coefficient:

$$C(x,y,t) = \frac{C_0 x}{4\sqrt{\pi D_l}} \exp\left(\frac{vx}{2D_l} - \beta t\right) \bullet \int_0^{t/R} \exp\left[-\left(\lambda R - \beta R + \frac{v^2}{4D_l}\right)\tau - \frac{x^2}{4D_l\tau}\right]\tau^{\frac{-3}{2}} \bullet \left[\operatorname{erf}\left(\frac{a-y}{2\sqrt{D_t\tau}}\right) + \operatorname{erf}\left(\frac{a+y}{2\sqrt{D_t\tau}}\right)\right] d\tau \qquad \text{(C-5)}$$

Plume lengths as a function of time using the Cleary and Ungs (1978) model are shown on Figure C-6. Domenico (1987) forecast plume lengths are shown for comparison; the difference between the Domenico model and the conservative version of the Cleary and Ungs (1978) model (no source attenuation; $\beta = 0$) is due to different assumptions in the mathematical formulations of the two models. The results how that source attenuation limits the downgradient extent of the plume to some degree but also results in retreat of the plume; rapid collapse is observed when the source attenuation half-life is on the order of three years.

Clearly, the source attenuation rate is critical in evaluating the time required for complete plume dissipation. However, this rate cannot be quantified easily from field data, particularly when the exponential source decay model is an idealization of the cumulative effect of a number of processes. However, constraints may be placed on the plume dissipation rate by evaluating the assumed residual hydrocarbon volume. The volume of hydrocarbon material in the dissolved state, as implied by the model, can be calculated by assuming the water flowing through a cross-section of the aquifer defined by the residual hydrocarbon width and assumed aquifer thickness equilibrates with the prescribed residual hydrocarbon concentration, corrected for source decay as a function of time. The implied cumulative residual hydrocarbon volumes derived from this calculation are shown on Figure C-7.

Given the release scenario at Building 637 and the residual hydrocarbon removal activities at the Site, a residual hydrocarbon volume of about 250–1,000 gallons may be realistic. Larger residual hydrocarbon volumes of several thousand gallons may not be realistic. If it is assumed that there is a decrease of half the residual TPH volumn every three to fifteen years ($t_{1/2}$ = 3–15years), then the plume may be expected to dissipate in several decades.

References

Busheck, T. E., D. C. Wickland, and D. L. Kuehne (1996), "Multiple lines of evidence to demonstrate natural attenuation of petroleum hydrocarbons," in *Proceedings from the Conference on Petroleum Hydrocarbons and Organic Chemicals in Ground Water*, National Ground water Association/API, Houston, Texas, November 13–15.

Chapelle, F. H., P. M. Bradley, D. R. Lovley, and D. A. (1996), "Vroblesky, Measuring rates of biodegradation in a contaminated aquifer using field and laboratory methods," *Ground Water*, **34(**4), 691–698.

Cleary, R. W., and M. J. Ungs (1978), *Groundwater pollution and hydrology, mathematical models and computer programs*, Water Resources Program, Princeton University, Princeton, N.J., Report 78-WR-15.

Domenico, P. A. (1987), "An analytical model for multidimensional transport of a decaying contaminant species," *Journal of Hydrology*, **91**, 49–58.

MacIntyre, W. G., M. Boggs, C. P. Antworth, and T. B. Stauffer (1993), "Degradation kinetics of aromatic organic solutes introduced into a heterogeneous aquifer," *Water Resources Research*, **20**, 4045–4051.

Rice, D. W., R. D. Grose, J. C. Michaelson, B. P. Dooher, D. H. MacQueen, S. J. Cullen, W. E. Kastenberg, L. E. Everett, and M. A. Marino (1995), *California Leaking Underground Fuel Tank (LUFT) Historical Case Analyses*, Lawrence Livermore National Laboratory, Livermore, Calif. (UCRL-AR-122207).

Wilson, J. T., G. Sewell, D. Caron, G. Doyle, and R. N. Miller (1995), "Intrinsic Bioremediation of Jet Fuel Contamination at George Air Force Base," in *Intrinsic Bioremediation*, R. E. Hinchee, R. E., J. T. Wilson, and D.C. Downey, Eds. (Battelle Press, Richland, Wash.), pp. 91–100.

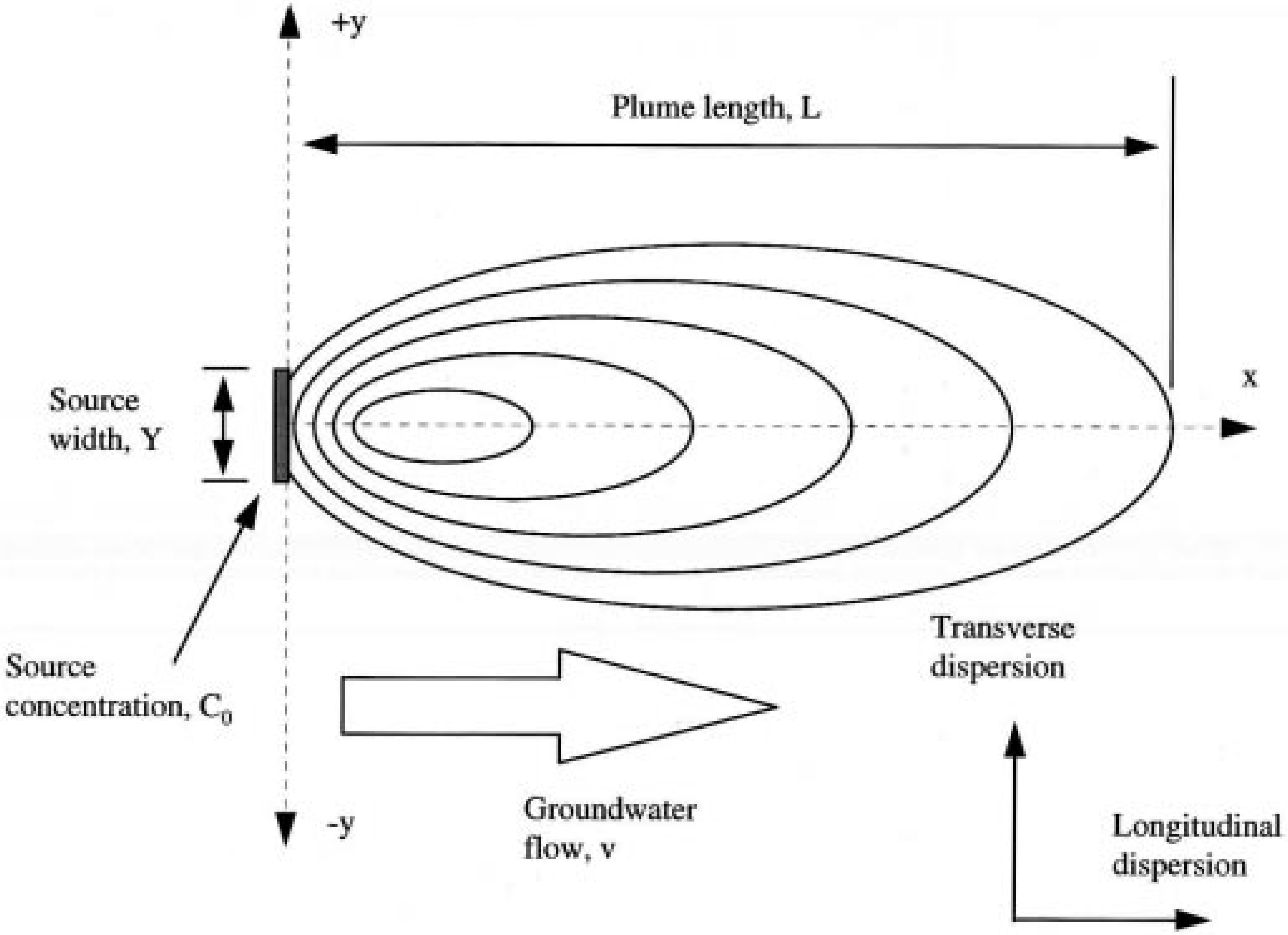

Figure C-1. Idealized plume model.

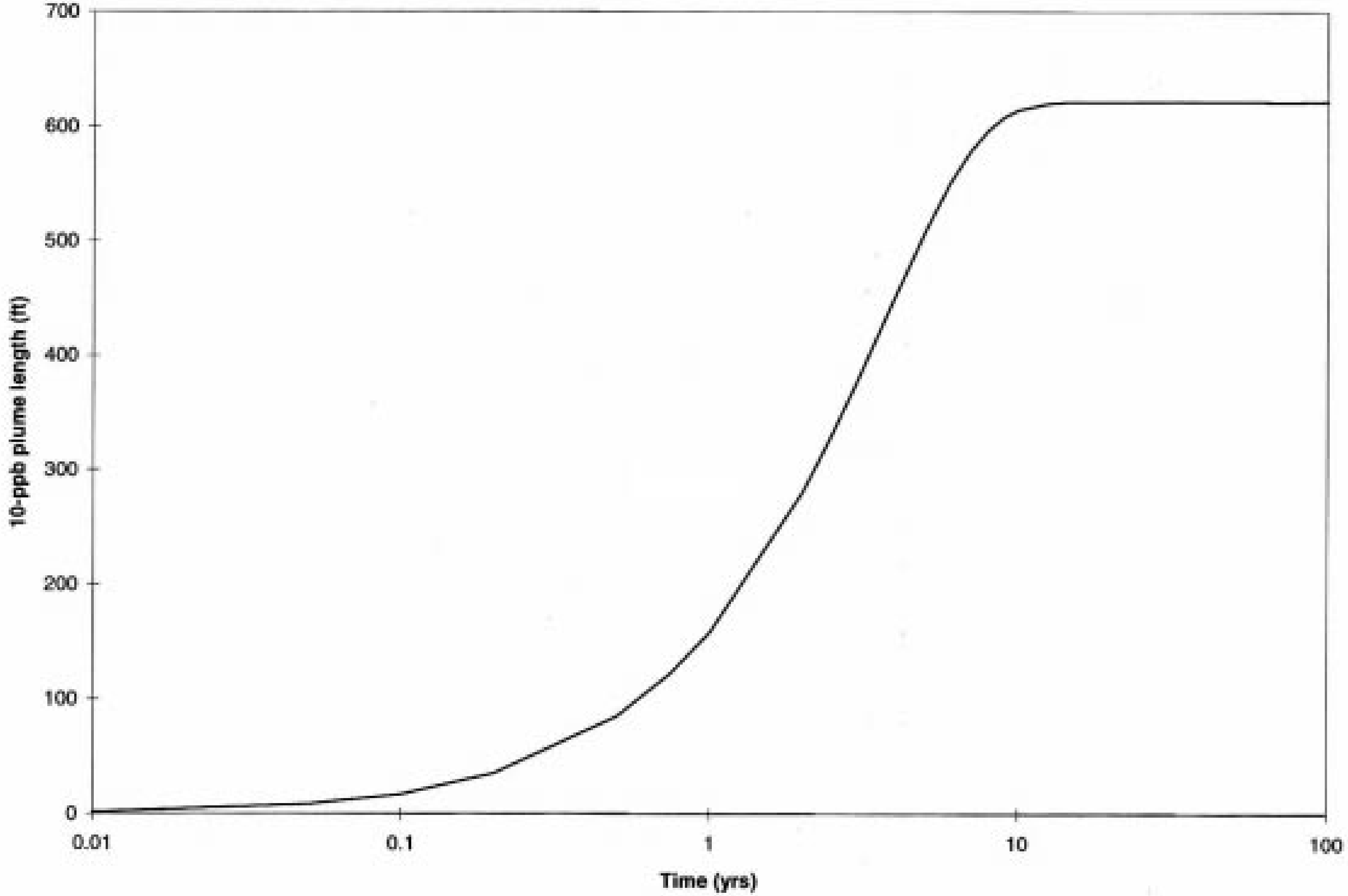

Figure C-2. Predicted gasoline range hydrocarbon plume length (as defined by the 10 ppb) according to the Domenico (1987) model, utilizing conservative or representative assumptions, supplemented by site data.

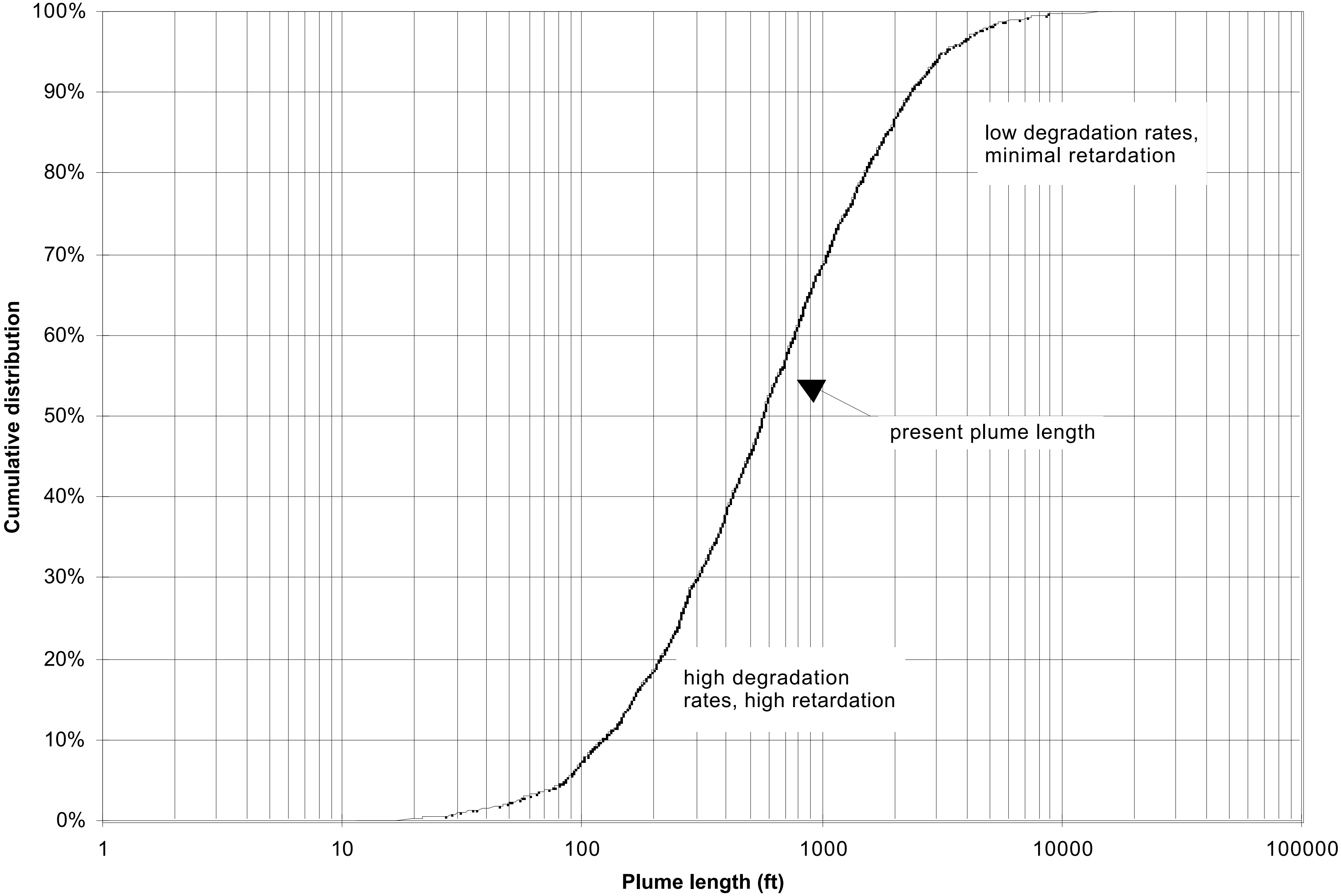

Figure C-3. Forecast distribution of hydrocarbon plume lengths (defined by the 10-ppb contour) estimated by Monte Carlo anlaysis.

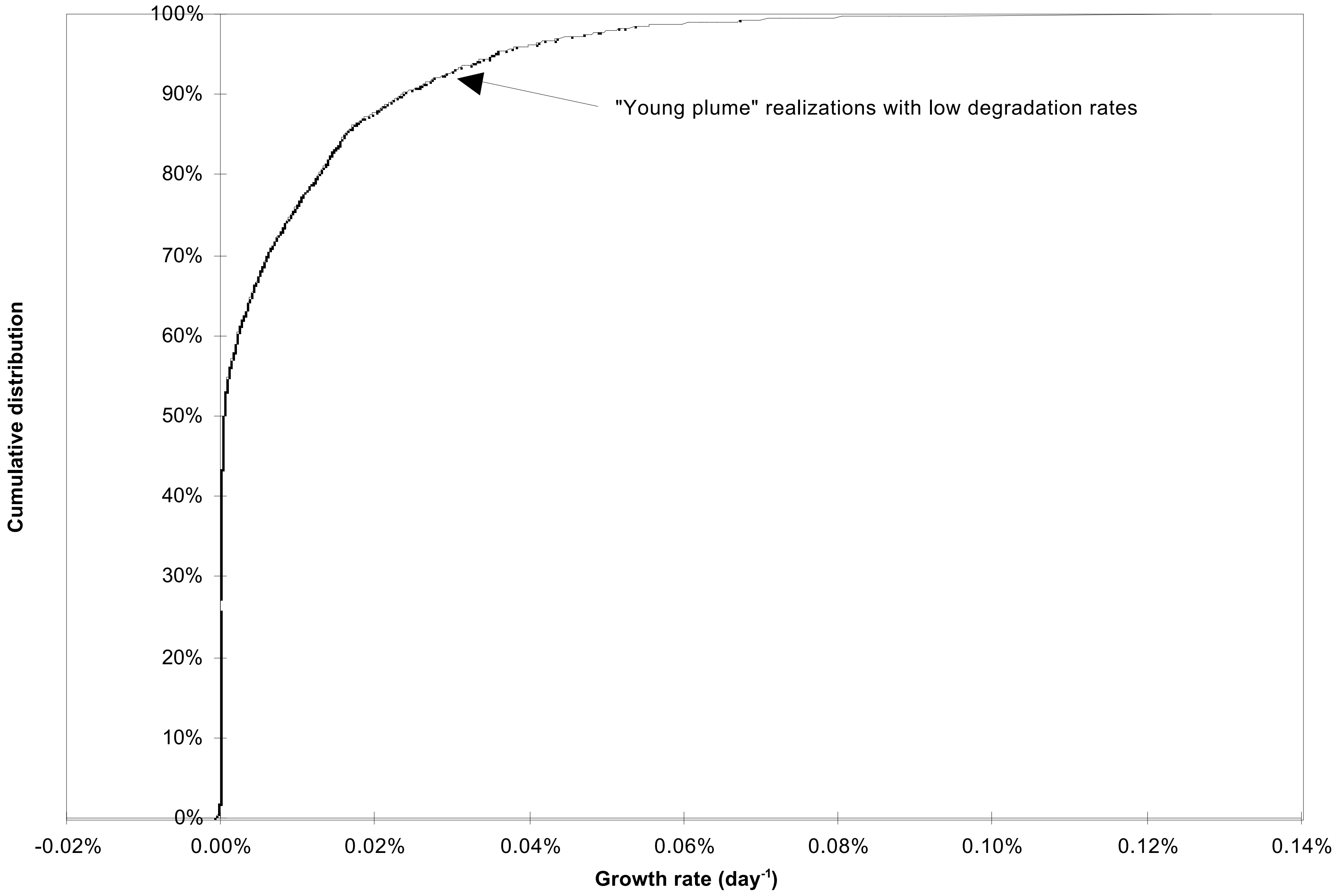

Figure C-4. Forecast probability distribution of normalized plume growth rates estimated by Monte Carlo analysis.

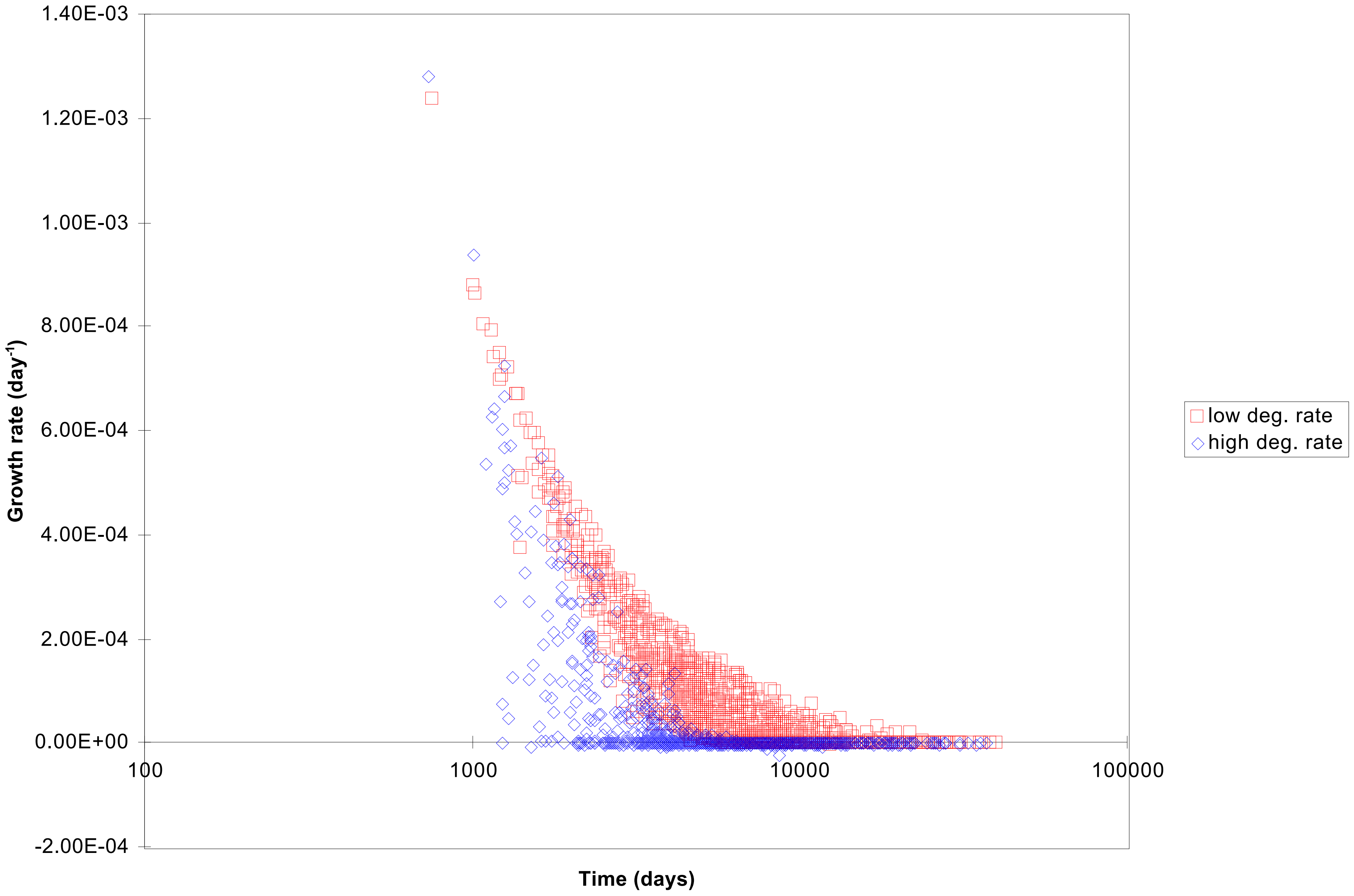

Figure C-5. Forecast growth rates as a function of time for low degradation rates (below the median value of 0.15% day-1) and high degradation rates (above median value).

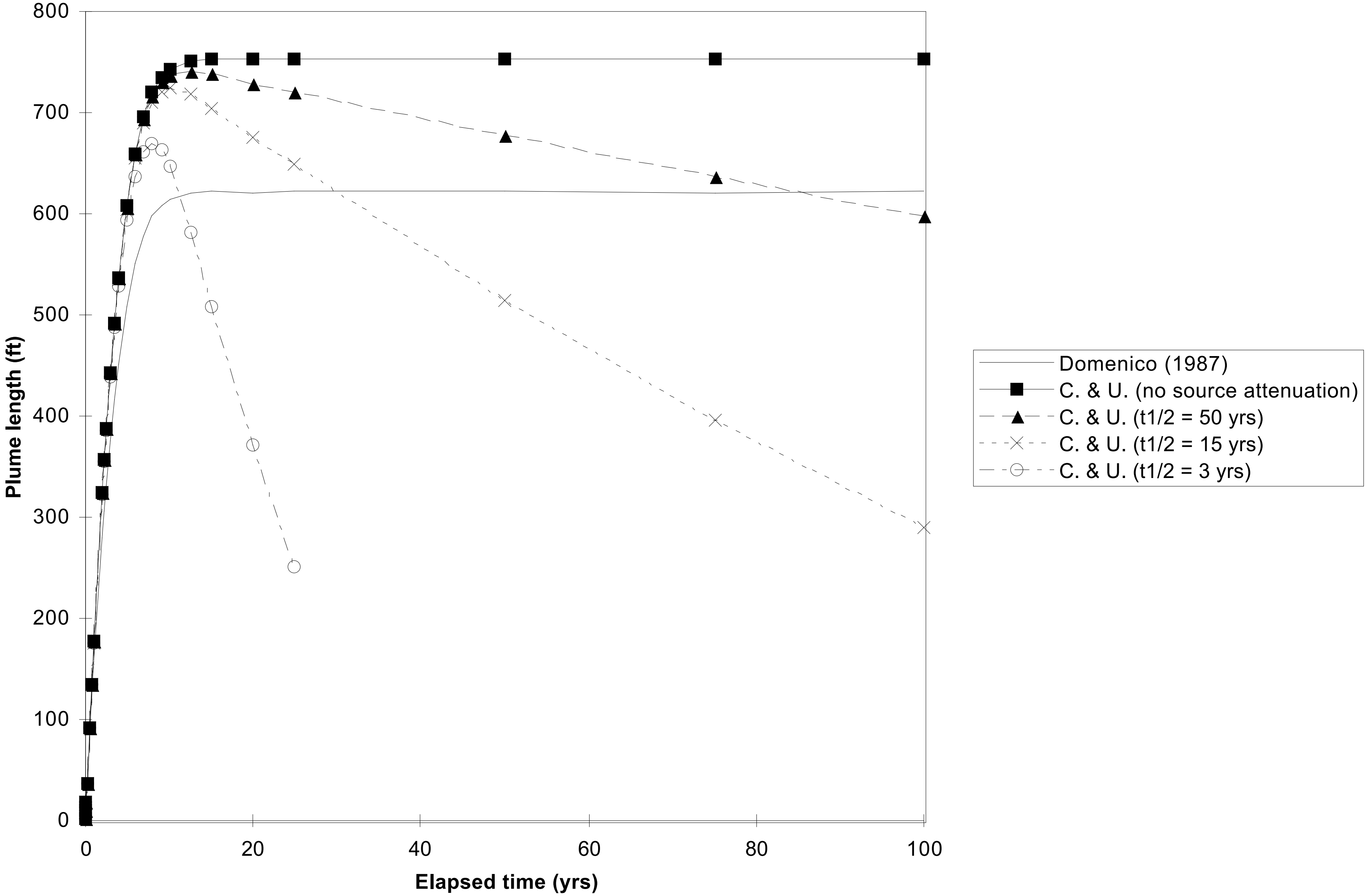

Figure C-6. Forecast hydrocarbon plumes lengths (as defined by the 10-ppb contour) as a function of time using the Cleary and Ungs (1978) solution. Domenico (1987) forecasts are shown for comparison.

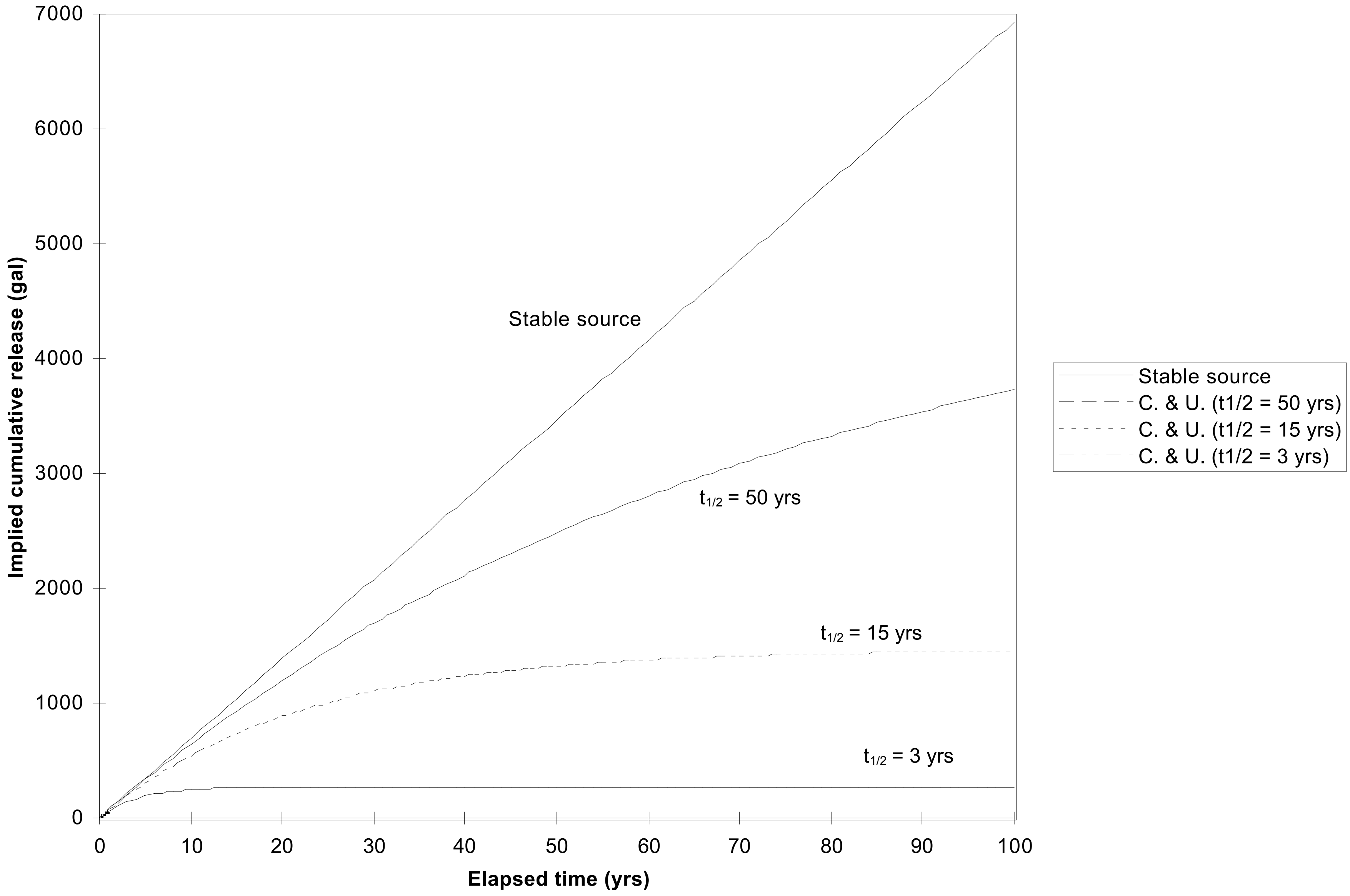

Figure C-7. Implied volumes (gallons of gasoline, assuming a liquid density of 0.8ng/cm3) corresponding to forecast plume lengths (Figure C-6),