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Department of Defense Petroleum Hydrocarbon Cleanup Demonstration Program Final Report:

Risk-Informed Decision Making at Petroleum Contaminated Sites

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Submitted to:

U.S. Navy, Southwest Division, Naval Facilities Engineering Command, San Diego, California
U.S. Air Force Center for Environmental Excellence, Environmental Restoration Directorate, Technology Transfer Division, Brooks Air Force Base, Texas
U.S. Army Corps of Engineers, Sacramento District, Sacramento, California
California State Water Resources Control Board, Sacramento, California

October 1998

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****Malcolm Pirnie Corporation, Emeryville, California
*****U.S. Environmental Protection Agency, San Francisco, California

Environmental Protection Department
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Executive Summary

Program Overview

This document summarizes the findings, conclusions, and recommendations resulting from a 24-month Department of Defense leaking (DoD) underground fuel tank (LUFT) cleanup demonstration program that focused on ten California military bases. Selection of sites for this demonstration program was coordinated through the California Military Environmental Coordination Committee Water Process Action Team. The Demonstration Program sites were selected to represent each branch of the military services with bases in California, and as many of the nine California Regional Water Quality Control Boards (RWQCBs) and California hydrogeologic settings where fuel hydrocarbon contaminant cleanup problems occur, as possible.

The sites selected and their corresponding RWQCB are:

- Barstow Marine Corps Logistic Center, Tank 325 Site (Lahontan RWQCB).
- Camp Pendleton Marine Corps Base, Area 43 Gas Station Site (San Diego RWQCB).
- Castle Air Force Base, Petroleum, Oils, and Lubricants Yard (Central Valley RWQCB).
- China Lake Naval Weapons Center, Navy Exchange Gas Station Site (Lahontan RWQCB).
- El Toro Marine Corps Air Station, Underground Storage Tanks 390A/B (Santa Ana RWQCB).
- George Air Force Base, Operable Unit 2 (Lahontan RWQCB).
- Port Hueneme Naval Construction Battalion Center, Navy Exchange Service Station Site (Los Angeles RWQCB).
- U.S. Army, Presidio of San Francisco, Building 637 area (San Francisco Bay RWQCB).
- Travis Air Force Base, North/South Gas Station Sites (San Francisco Bay RWQCB).
- Vandenberg Air Force Base, Base Exchange Gas Station Site (Central Coast RWQCB).

The primary goals of the DoD LUFT Cleanup Demonstration Program are:

1. Evaluate how risk-based cleanup can be applied at DoD sites within the current context of California regulations.
2. Demonstrate the evaluation and appropriate application of passive bioremediation to manage residual hydrocarbons.
3. Provide training to California DoD LUFT cleanup managers in the application of risk-informed cleanup approaches and the lessons learned.

As part of the demonstration program, an expert panel composed of scientific professionals from universities, private industry, and Federal regulatory agencies was formed to provide program oversight and prepare recommendations to DoD regarding LUFT cleanup approaches.

Background

Regulatory Background

Numerical groundwater cleanup goals are specified within California Laws and Regulations. If the probable beneficial use as specified within Basin Plans is municipal (MUN), the cleanup goals are restricted to maximum contaminant levels (MCLs) or background. Regulations and policies require considerations of reasonableness, practicality, and economic feasibility along with protection of human health, the environment, and beneficial uses of resources.

Risk-Informed Cleanup

As part of the DoD LUFT Cleanup Demonstration Program, the Expert Committee (EC) has applied a form of risk-based cleanup referred to as risk-informed decision making. This new terminology is used also to emphasize the fact that corrective action decisions are made with input from stakeholders representing both local and state concerns, and that the inputs to the decision-making process include: (1) potential health impacts, (2) resource damage and effect on water supply, (3) long-term fate of contaminants, (4) cost of remediation options (if necessary), (5) aesthetics, and (6) other relevant factors. Inherent in all of these factors are interrelated considerations of contaminant longevity and migration, projected land and resource use, and possible land and resource use restrictions, and the reliability and uncertainty of existing data. Corrective actions taken using a risk-informed cleanup process should (1) improve the situation, (2) not foreclose future options, and (3) minimize societal strain.

Comparison of DoD and Private/Commercial LUFT Sites

The characteristics of the ten DoD facility sites in the DoD LUFT Cleanup Demonstration Program spanned a wide range of hydrogeologic and petroleum release conditions and issues, and were generally representative of DoD LUFT sites in California. When compared to typical private/commercial LUFT sites, the EC found some characteristics of the DoD demonstration sites to be unique and critical to the risk-informed cleanup process. These characteristics included the following:

- DoD LUFT sites generally occupy small portions of much larger DoD facilities.
- The types of DoD releases encompass a wider range of petroleum products than at typical UST release sites (e.g., light jet fuels -> gasoline -> heavy bunker fuels); although in many cases, only a single fuel type is stored at any given DoD LUFT site.
- The volumes of petroleum products transported, stored, and dispensed over time can be much larger than at typical non-DoD UST sites; therefore, quantities of petroleum liquids released can be very large in comparison with typical UST release sites, even when the site is a service station located on a DoD facility.
- Off-site properties are not always affected by the petroleum release, as is the case for most non-DoD petroleum release sites.

- At operating DoD facilities it may be easier to implement land use restrictions (often associated with natural attenuation corrective action plans) than at typical UST petroleum release sites.
- During the time period that corrective action decisions are being made, future land use may be uncertain at facilities that are, or will be closed; however, it is common for land use restrictions to be in place at the time of property transfer.
- There is typically much more public participation and oversight for cleanups at DoD facilities than at typical UST sites.
- The lead regulatory agency is not always the same agency that would typically oversee commercial/private UST cleanups in the area.
- Cleanup costs at DoD petroleum release sites can exceed the costs for typical UST site cleanup by at least an order of magnitude.

Conceptual Model of Fuel Hydrocarbon Releases

The idealized physical conceptual model of a fuel hydrocarbon groundwater plume consists of two essential elements. The first element is the nature of the residual hydrocarbon material providing mass to the plume. The residual hydrocarbons can be characterized as light non-aqueous phase liquids, either as free-product lenses floating on the capillary fringe, or as discrete ganglia entrapped within the vadose zone or even below the water table. The second element is the dissolved plume extending downgradient of the residual hydrocarbon area. The dissolved plume is affected by advective and dispersive transport, retardation, and biodegradation. Cleanup approaches that rely on natural attenuation processes, particularly biodegradation (passive bioremediation), may limit the downgradient migration of the dissolved plume. The interplay of the two elements leads to the concept of a steady-state plume existing under dynamic equilibrium conditions, where the mass influx of dissolved contaminants from residual hydrocarbons is balanced by mass loss via biodegradation, integrated across the spatial extent of the plume.

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. Appropriate use of passive bioremediation as a remedial alternative requires the same care and professional judgment as the use of any other remedial alternative. Passive bioremediation actively destroys fuel hydrocarbon mass in the subsurface, limiting the spatial extent of the groundwater plume in the short term while eventually remediating the contamination over longer time periods. Evidence demonstrating the impact of passive bioremediation processes may be classified as primary or secondary in nature. Primary evidence pertains to statistically significant trends in concentration data which are consistent with plume stability or decline over time. Such data are sparse at DoD sites (and most LUFT sites in general) because of relatively short monitoring time scales in comparison to the age of the plumes. Secondary evidence consists of the measurable impact of passive bioremediation processes on the groundwater geochemistry. Spatial variability in concentrations of species such as dissolved oxygen, nitrate, sulfate, ferrous iron, manganese, methane, and bicarbonate alkalinity are known to be observed at LUFT sites from numerous past studies. At each of the sites in the DoD Demonstration Program with sufficient groundwater geochemical data, distributions of these species are consistent with passive bioremediation. Indeed, the quantitative analyses of such data, in conjunction with site hydrogeologic information, can be used to assess passive bioremediation rates.

The anticipated time-to-cleanup was a key issue at each of the sites. From a technical perspective, estimating the time to cleanup requires a determination of residual hydrocarbon product mass and attenuation rate. From a policy perspective, if cleanup within a specified time frame is a remedial goal, then reconciliation of the required time frame with physical laws of contaminant behavior must be addressed.

Forecasting the time required for plume collapse and cleanup requires estimating the time scale of residual hydrocarbon depletion. For engineered residual hydrocarbon removal, this requires an estimate of mass removal rates as a function of time. For natural depletion of the residual hydrocarbons, this requires estimates of light non-aqueous phase liquid (LNAPL) dissolution rates into groundwater as well as volatilization rates into the vadose zone. An accurate estimate of residual LNAPL volume is also necessary. From a characterization viewpoint, much of this additional information is extremely difficult to obtain or to estimate accurately. As a result, the time scale required for plume collapse, by natural source weathering and/or engineered source removal, often cannot be predicted with high confidence.

Typical residual hydrocarbon removal technologies at LUFT sites include free-product removal, soil vapor extraction, bioventing, and over-excavation. Several factors should be considered in the selection of residual hydrocarbon zone treatment technologies:

- If the remedial goal is only to ensure plume stabilization, then treatment of the residual hydrocarbon zone soils is irrelevant.
- If the remedial goal is one of plume collapse within a decade or stabilization of the plume within a small area, then active residual hydrocarbon zone treatment will likely be required.
- Each active remedial technology has a practical limitation of effectiveness and so technologies must often be applied in a sequence, with passive bioremediation being the final step in the treatment train.
- LNAPL extraction efforts are self-limiting in effectiveness. Recovery decreases with time because the removal of the most mobile portion of the LNAPL phase reduces the mobility of the remaining material. This occurs when capillary forces exceed the driving forces associated with the LNAPL gradient. Termination of actively engineered removal of free or residual product may be appropriate when the mass removal rate either reaches asymptotic levels or declines to levels where only *de minimus* amounts of product are being removed. Alternative product removal technologies, such as high vacuum extraction or steam injection, should be evaluated in those situations where such high cost is warranted.
- Decision-makers should carefully weigh the benefits and costs of active remediation, and should recognize that active remediation systems by themselves rarely achieve drinking water standards in short time frames at groundwater-impacted sites.
- The main benefit of active remediation at most LUFT sites is a reduction in the uncertainty risk associated with the site and the time frame over which restoration of the site will occur.

Findings

Risk-Informed Cleanup at DoD LUFT Cleanup Demonstration Program Sites

While alternative site-specific cleanup standards are not routinely allowed within California's regulatory frame work, risk-informed decisions are routinely made by regulatory staff. These decisions include acceptable time for cleanup, and how much data is required before no-further-action is permitted at DoD LUFT sites. Regional boards are able to issue no-further-action letters to responsible parties before reaching MCLs or background. The decision to issue a no-further-action letter or require further active remediation is typically made based on an evaluation of the time-frame for anticipated beneficial use and a balance between practical and economic considerations.

No-further-action may be permitted in DoD LUFT cases where there are no risks to human health or the environment, and where passive bioremediation has shown to be destroying hydrocarbons at a rate sufficient to reach MCLs or background prior to anticipated beneficial use, and where institutional controls exist to prevent exposure during the time passive remediation is occurring.

There is no clear coordinated guidance regarding when no-further-action is permitted at a site. Moreover, there is a broad application of municipal beneficial use (MUN) to groundwater, even if the groundwater is unlikely to be used. This broad designation of MUN to groundwaters gives regulators the flexibility of requiring strict cleanup numeric goals and then relaxing active cleanup requirements when regulatory staff find the uncertainty in achieving the cleanup goals acceptable. This flexibility results in inconsistent risk management practices between sites when a variety of case workers are involved, each with a different interpretation of what may be acceptable in similar circumstances.

Conceptual Model Elements

The development of a site-specific conceptual model is a critical component in risk-informed cleanup. A conceptual model is made up of a series of hypotheses that guide characterization. A well defined conceptual model of a site contains sufficient information to: (1) identify sources of the contamination, (2) determine the nature and extent of the contamination, (3) identify the dominant fate and transport characteristics of the site, (4) specify potential exposure pathways, and (5) identify potential receptors that may be impacted by the contamination. Regional and local shared historical data can be used to develop site conceptual model hypothesis, particularly with regard to the fate and transport characteristics of the site.

In general, DoD LUFT site conceptual models were often not as well formulated as the EC had expected. The Expert Committee observed that during site briefings, a clear set of hypotheses regarding the nature and extent of the release and the factors that control the released petroleum hydrocarbon movement was often not provided or could be improved. Further, conceptual models were often recreated with each new contractor.

Management of Residual Hydrocarbons at DoD LUFT Cleanup Demonstration Program Sites

Despite the presence of residual FHCs at all the DoD Demonstration Program Sites, risks to human health and the environment at these sites are minimal. The plumes at the Demonstration Program sites are likely to have already stabilized in terms of downgradient extent. The depletion of existing residual hydrocarbons of the compounds of concern, such as benzene, through natural weathering processes (dissolution, volatilization) at many of the sites will probably require several decades, perhaps even a century. Regional Water Quality Control Boards have expressed concerns that this time frame exceeds a reasonable institutional planning horizon and thus active remediation of residual hydrocarbons may be needed to reduce the uncertainty in the risk to future users of the impacted ground water. The EC agrees that a general best management practice for free product is to remove that mass that is relatively easy to extract. Termination of actively engineered removal of free or residual product may be appropriate when the mass removal rate either reaches asymptotic levels or declines to levels where only *de minimus* amounts of product are being removed. Alternative product removal technologies, such as high vacuum extraction or steam injection, should be evaluated in those situations where such high cost is warranted. Regional Water Quality Boards are encouraged to develop protocols for determining when active product removal efforts should be abandoned.

Recalcitrant Fuel hydrocarbon Compounds

It is important to note that risk informed decision making is equally applicable to sites with and without MTBE present. The decisions regarding corrective action are, however, likely to be different at sites with and without MTBE. Knowledge of MTBE’s chemical properties, fate and transport evaluations, site properties, and definition of possible pathways and receptors will lead to appropriate corrective action decisions.

Should active remediation of MTBE be required at a site, most of the existing remediation tools used to remediate BETX releases can successfully be applied to deal with MTBE. MTBE may be expected to move at the same average rate as the ground water. In addition, MTBE appears to degrade at a rate significantly slower than benzene or the other aromatic compounds of concern at a fuel hydrocarbon release. Under some geochemical conditions, not yet fully understood, MTBE may not degrade at all. As a consequence, those sites that previously may have been potential candidates for application of monitored natural attenuation may no longer meet the necessary conditions for this remedy, if MTBE is present.

Recommendations

Recommendation 1: Consistent guidance should be developed by the State of California to define target time frames for achieving remedial goals.

State-wide guidance should consider current and future land use, as well as the implementability of relevant land-use restrictions. Target time frames should be set for both (1) ensuring contaminant stabilization (i.e., no further spreading/migration of contaminant), and (2) final closure of the site (i.e., achieving state-mandated target cleanup levels).

Recommendation 2: State-wide guidance is needed that formally recognizes that achieving low μg/L concentrations is not practicable in the short term (<10 years) at most sites with groundwater impacted by fuel hydrocarbons.

Definition of cleanup times must take into account basic constraints imposed by natural laws governing the transport and natural degradation process of petroleum hydrocarbons. The actual time required to reach groundwater cleanup goals are determined by these laws and limitations on residual hydrocarbon attenuation rates, through either active or passive processes, will practically constrain the time frame to achieve MCL cleanup goals. Guidance on the definition of what is reasonable and what is not technically or economically feasible would be an appropriate first step.

Additionally, recognition is needed that sites should be transitioned to remediation by natural processes at some point following implementation of active remediation options as appropriate. Guidance for determining the appropriate stage of corrective action for this transition is needed.

Recommendation 3: DoD should develop and use a site conceptual model as the focal point of the corrective action decision-making process at each site.

Each site should identify a keeper of the conceptual model. A commonly accessible data base should be established to promote shared historical case data and foster development of conceptual model hypotheses. Sites should share data to reduce uncertainty. The question of site characterization adequacy should always be linked back to the uncertainty in the site conceptual model.

Recommendation 4: DoD should develop better approaches for estimating residual petroleum hydrocarbon longevity.

As it will play an important role in risk-informed decision making, and since current approaches are inadequate, DoD should develop a better approach for estimating residual petroleum hydrocarbon longevity. Free product and residual hydrocarbon recovery should not be attempted beyond what can be reasonably expected given natural subsurface constraints upon the recovery process. As part of the National Test Site Program, DoD needs to do research to be able to better project residual hydrocarbon longevity under scenarios involving natural conditions, and partial remediation followed by natural attenuation.

1. Program Overview and Methods

1.1. The DoD LUFT Cleanup Demonstration Program

This document summarizes the findings, conclusions and recommendations resulting from a 24-month Department of Defense (DoD) leaking underground fuel tank (LUFT) cleanup demonstration program that focused on ten California military bases. In June 1994, the California State Water Resource Control Board (SWRCB) contracted with the Lawrence Livermore National Laboratory/University of California (LLNL/UC) to study the cleanup of Leaking Underground Fuel Tanks (LUFTs) in California. The LLNL/UC Report, *Recommendations to Improve the Cleanup Process for California's Leaking Underground Fuel Tanks,* concluded that risk-based corrective action (RBCA) provides a practicable framework within which corrective action decisions are based on consideration of current and future risk of adverse impact to humans, resources, and ecological receptors (Rice et al., 1995a). The LLNL/UC LUFT Recommendations Report also recommended that a series of LUFT sites be identified where the application of risk-based LUFT cleanup approaches could be demonstrated.

As a result, ten DoD sites were selected to participate in a DoD Petroleum Hydrocarbon Cleanup Demonstration (PHCD) Program. This program will be referred to as the DoD LUFT Cleanup Demonstration Program. 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, and as many of the California Regional Water Quality Control Boards (RWQCBs) and diverse hydrogeologic settings in California where fuel hydrocarbon (FHC) contaminant cleanup problems occur as possible. The sites selected and their corresponding RWQCB are:

- Barstow Marine Corps Logistic Center, Tank 325 Site (Lahontan RWQCB).
- Camp Pendleton Marine Corps Base, Area 43 Gas Station Site (San Diego RWQCB).
- Castle Air Force Base, Petroleum Fuel Farm Area (Central Valley RWQCB).
- China Lake Naval Weapons Center, Navy Exchange Gas Station Site (Lahontan RWQCB).
- El Toro Marine Corps Air Station, Underground Storage Tanks 390A/B (Santa Ana RWQCB).
- George Air Force Base, Operable Unit 2 (Lahontan RWQCB).
- Port Hueneme Naval Construction Battalion Center, Navy Exchange Service Station Site (Los Angeles RWQCB).
- U.S. Army, Presidio of San Francisco, Building 637 area (San Francisco Bay RWQCB)
- Travis Air Force Base, North/South Gas Station Sites (San Francisco Bay RWQCB).
- Vandenberg Air Force Base, Base Exchange Gas Station Site (Central Coast RWQCB).

1.2. Program Goals

The first goal of the DoD LUFT Cleanup Demonstration Program is to evaluate how risk-based cleanup can be applied at DoD sites within the current context of California regulations. At the heart of the DoD LUFT Cleanup Demonstration Program is the assumption that risk-based cleanup and remediation approaches, including risk-informed decision making, can be integrated within the existing California regulatory framework without changing the underlying philosophy. The ten DoD LUFT Cleanup Demonstration Program sites provide specific examples of LUFT release sites which can be used to evaluate this hypothesis.

The LLNL/UC Report also recommended that passive bioremediation (natural attenuation) be considered as an alternative to more active engineered remediation approaches at LUFT sites. Thus, another goal of the DoD LUFT Cleanup Demonstration Program was to examine how this option might effectively and appropriately be utilized within a risk-based approach that was consistent with existing policies and regulations. Included as part of this DoD LUFT Cleanup Demonstration Program goal is the demonstration of techniques to measure and evaluate site-specific passive bioremediation processes. The evaluation of passive bioremediation as a potential remediation process considered not only the traditional fuel hydrocarbons such as benzene, toluene, xylene, but also included the fuel oxygenate, methyl *tertiary* butyl ether (MTBE).

A final DoD LUFT Cleanup Demonstration Program goal is to provide training to California DoD LUFT cleanup managers in the application of risk-informed cleanup approaches and the lessons learned as a result of the DoD LUFT Cleanup Demonstration Program.

1.3. Program Expert Committee

To oversee this process and provide guidance to sites participating in the DoD LUFT Cleanup Demonstration Program, a committee of experts was formed. This panel is comprised of scientific professionals from universities, private industry, and Federal regulatory agencies. The Expert Committee (EC) provides professional interpretations and recommendations regarding the application of risk based LUFT cleanup approaches and closures at demonstration sites. The EC members selected to evaluate the DoD LUFT Cleanup Demonstration Program sites are:

- Dr. Stephen Cullen, UC, Santa Barbara, Institute for Crustal Studies, 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 with 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 the National Academy of 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, Environmental Scientist, 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 Director and Expert Committee Chairman.
- Mr. Matthew Small, U.S. EPA Region IX, Hydrogeologist; Co-Chairman of U.S. EPA Remediation by Natural Attenuation Committee, with expertise in risk-based corrective action and passive bioremediation.

It should be recognized that the Expert Committee membership represents a range of professional opinions and biases. For this reason, documents prepared by the expert committee were reviewed and discussed by all the members of the expert committee and any findings, conclusions, and recommendations are reached through consensus.

1.4. Program Steps

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

Step 1: An initial site scoping meeting was held with each site's staff, regulators, and DoD LUFT Cleanup Demonstration Program representatives to discuss site conceptual model and identify and discuss pathways and receptors of concern. Guidance was provided to assist the site staff and contractors in preparing a site-specific data package which was used to brief the DoD LUFT Cleanup Demonstration Program EC members.

Step 2: In parallel with the initial site scoping, training in risk-based cleanup approaches was offered for DoD LUFT Cleanup Demonstration Program participants.

Step 3: The DoD LUFT Cleanup Demonstration Program EC members next visited each site and were briefed on the site's characterization, conceptual model, and pathways and receptors of concern. A site tour was included in this briefing. A lead EC member was designated for each site. Following each site visit, the EC reviewed and identified additional data needed to apply a risk-based LUFT cleanup approach. A site characterization letter report was prepared containing recommendations for further data collection, if needed. Sampling and monitoring procedures to support evaluations of passive bioremediation processes which may be occurring at the site were also identified.

Step 4: Once the best available data had been provided, the EC members considered how a risk-based cleanup approach may be applied to the site and prepared its recommendations for an appropriate risk-management strategy at the site and the set of actions needed to achieve site closure. Included in this process was an evaluation of the appropriate use of natural attenuation as a remedial alternative at the site. Whenever possible, an estimate of the time to cleanup and the uncertainty associated with this estimate was also made.

The EC's risk-based site-specific assessment of appropriate fuel hydrocarbon cleanup strategies was provided in draft to each site to provide an opportunity for site regulators and other stakeholders to comment. After considering the offered comments, the EC members prepared a final site-specific risk-management strategies report which was delivered to each site.

Step 5: Finally, once all the sites had been evaluated, the EC prepared this document, which is a summary of DoD LUFT Cleanup Demonstration Program findings and lessons learned in applying risk-based cleanup at California DoD sites, including conclusion and recommendations to both the DoD and SWRCB. In addition to this document, the DoD LUFT Cleanup Demonstration Program lessons learned are provided in the DoD *Risk Execution Strategy for Clean-Up of the Environment* implementation guide (RESCUE) Road Map) that can be accessed by DoD sites through the world-wide-web. A discussion of the cost savings using risk-based cleanup protocols is provided in a separate document.

2. Background

2.1. Regulatory Framework

One of the key issues that faced the DoD LUFT Cleanup Demonstration Program is whether or not risk-based decision making can be integrated into the existing California regulatory framework without significant changes in the underlying regulations and policies of the SWRCB/RWQCBs. California USTs are regulated through a framework of laws, regulations, and state, regional, and local policies. The California Water Code is the law from which regulations and policies are derived. SWRCB resolutions are policies used to implement the Water Code.

California water resources are managed by the nine RWQCBs. The designation of probable beneficial uses and associated cleanup goals to meet these beneficial uses fall within the current discretion of each RWQCB. The California Water Code requires the RWQCB's to protect beneficial uses into the future, not just for present short-term scenarios (non-degradation policy).

The Porter–Cologne Water Quality Control Act, Chapter 1 (commencing with Section 13000), Division 7, of the California Water Code, stipulates to state and regional water boards that "… those activities and factors (that) may affect the quality of the waters of the state shall be regulated to attain the highest water quality which is reasonable; considering all demands being made and to be made on those waters and the total values involved, beneficial and detrimental, economic and social, tangible and intangible …."

Because different regions have a range of hydrogeologic settings and water management practices and uses, the SWRCB and RWQCBs are required by law to manage the state's water resources through a policy that considers "... factors of precipitation, topography, population, recreation, agriculture, industry and economic development (that) vary from region to region within the state, and that the statewide program can be most effectively administered regionally, within a framework of statewide coordination and policy (California Water Code, Chapter 1, Section 13000, Division 7)."

The RWQCBs develop Regional Basin Plans to establish the present and probable beneficial uses of water within their regions, and these plans are subject to State Board policies during the formulation of water quality objectives and beneficial uses. According to Section 13241 of the

California Water Code, the factors that RWQCBs should consider in setting water quality objectives "... shall include, but not necessarily be limited to, all of the following:

1. Past, present, and probable future beneficial uses of water,
2. Environmental characteristics of the hydrographic unit under consideration, including the quality of water available thereto,
3. Water quality conditions that could reasonably be achieved through coordinated control of all factors which affect water quality in the area,
4. Economic considerations,
5. The need for developing housing in the region, and
6. The need to develop and use recycled water."

SWRCB Resolution 88-63, known as the Sources of Drinking Water Policy, requires a broad application of the municipal (MUN) designation to groundwaters. The SWRCB determined that any aquifer that could produce over 200 gallons per day and had less than 3,000 mg/L total dissolved solids would suffice as a "potential" source of drinking water. As a result, with few exceptions, bodies of groundwater in the state are regulated as MUN water quality. RWQCB basin plans specify maximum contaminant levels (MCLs) as protective of groundwater with a MUN designation. MCLs are typically fixed numerical concentration standards specified within laws and regulations. SWRCB Resolution 92-49 states that the setting of cleanup concentrations above background shall not result in water quality less than that prescribed in adopted plans and policies, e.g., basin plans.

SWRCB Resolution 68-16, known as the Non-Degradation Policy requires that waters that are of higher quality than the water quality objectives within a basin plan must be maintained at the higher quality. Through the interpretation of this resolution, cleanup standards are broadly applied to all points within a groundwater basin.

Resolution 68-16 also specifies that cleanup requirements assure that the highest water quality consistent with the maximum benefit to the people of the state will be maintained. Through Resolutions 88-63 and 92-49, the consideration of maximum benefit is limited to the range between MCLs and non-detect for most groundwater basins in the state.

It is important to note that the broadly applied cleanup goals, such as MCLs, are themselves risk-based in nature; potential health impacts, aesthetic factors, and technology limitations are considered in their development. At issue here are two questions: (a) "Is it reasonable and practicable to broadly apply these fixed cleanup standards?", and (b) "How can risk-based cleanup decision making be incorporated within the existing regulatory framework?"

2.2. Risk-Informed Cleanup

As part of the DoD LUFT Cleanup Demonstration Program, the EC has applied a form of risk-based cleanup referred to as risk-informed decision making. In general, risk-based cleanup decision making involves the following activities:

1. A rapid assessment of the urgency of response based on considerations of the possible time and severity of impact; this helps to quickly identify appropriate initial response actions

(abatement, containment, monitoring, etc.) and can help regulatory staff prioritize/manage their case loads.

2. A determination of whether or not site conditions pose an unacceptable risk to human health, ecosystems, or the beneficial use of resources.
3. If conditions do pose an unacceptable risk, defining remedial goals for the site. These include both cleanup concentration goals and a target time frame within which these cleanup goals should be achieved.

Risk-based corrective action (RBCA) decision making applied to LUFT releases has received considerable attention on the national level and is being promoted by U.S. EPA. Many states are re-evaluating their policies and guidelines, and a considerable investment in the training of state regulators has been made.

RBCA can refer to risk-based corrective action decision making in general, or it can also refer to the specific framework proposed in the ASTM Guide to Risk-Based Decision Making at Petroleum Release Sites (1995). To avoid confusion, in this document we use the term "risk-informed decision making." This new terminology is used also to emphasize the fact that corrective action decisions are made with input from stakeholders representing both local and state concerns, and that the inputs to the decision-making process include: (a) potential health impacts, (b) resource damage and effect on water supply, (c) long-term fate of contaminants, (d) cost of remediation options (if necessary), (e) aesthetics, and (f) other relevant factors. During risk informed decision making, cleanup goals relating to health and or socioeconomic risks are set with input from stakeholders representing both local and state concerns. A remedy is selected that balances costs with achieving cleanup goals and improves the situation. See Appendix A for further information on the selection of remedial goals.

Inherent in all of these factors are interrelated considerations of contaminant longevity and migration, projected land and resource use and possible land and resource use restrictions, and the reliability and uncertainty of existing data. Each of these is discussed briefly below.

An understanding of contaminant migration potential can be gleaned from a combination of monitoring and predictive modeling. Given the experience gained over the past decade, our ability to assess contaminant migration potential is fairly good. For example, an important risk-informed decision-making input is the observation resulting from both the *California Leaking Underground Fuel Tank (LUFT) Historical Case Analysis* (Rice et al., 1995b) study and a study of the *Extent, Mass, and Duration of Hydrocarbon Plumes from Leaking Petroleum Storage Tank Sites in Texas* (Mace et al., 1997) that dissolved benzene plumes do not typically extend more than about 300 ft beyond the downgradient edge of the source zone, unless unusual hydrogeologic conditions exist at the site. Equally important is the uncertainty associated with dissolved MTBE plume migration. With respect to source longevity, a critical input to risk-informed decision making is the knowledge that our ability to predict source longevity under natural conditions is limited, and it is likely that source removal by natural processes may occur very slowly over decades at most sites.

Land and resource use is another of the key underlying factors that will affect risk-informed decision making. First, the severity and magnitude of potential adverse impacts will be different for different land use options (e.g., residential, commercial/industrial, recreational, etc.). Second, land use restrictions and institutional controls can be used to eliminate the potential for risks from pathways. Risk-informed decision making considers the strength of institutional controls, and how it might change in the future for a site with long contaminant longevity.

The third underlying factor is the uncertainty and reliability of the available data. There generally is a balance between uncertainty and the benefit of further data collection and characterization during risk-informed decision making. Uncertainties in size and location of residual hydrocarbons, site-specific hydrogeology, geochemistry, and natural degradation processes all contribute to uncertainty in the magnitude and time-scale of future risk.

Conservative assumptions in selecting models and their parameters are often used to address uncertainty. By compounding conservative assumptions, it is assumed that safety margins are maintained. A difficulty with using conservative assumptions to address uncertainty is that efforts may be misdirected towards sites with large uncertainties, but with potentially low risks, instead of towards sites with better known, but potentially higher risks. To avoid compounding assumptions, bounding estimates of parameters and probabilistic approaches have been used during the demonstration of modeling to support risk-informed decision making. A probabilistic approach provides an estimate of the uncertainty associated with the key decision- making elements such as time to reach cleanup goals. A safety margin can then be established relative to the uncertainty and to the best estimate of risk.

During risk informed decision making, monitoring is used to reduce uncertainty, both in the characterization of the site and in the likelihood that an inappropriate decision has been made. For example, detailed spatial characterization is not warranted and a higher degree of uncertainty is acceptable at sites where more robust engineered treatment systems (e.g., pump and treat, soil vapor extraction) are to be used. Uncertainties in future projections of source longevity and migration potential can be balanced by continued compliance monitoring requirements and contingency action plans. If the decision is to use natural attenuation, monitoring is used to confirm or improve the predicted attenuation rates. In either active or passive remediation, if new information indicates that the remedy will not achieve the cleanup goal, then both the remedy and the cleanup goal can be reconsidered. It may be that a different remedy is required, or it may be that the cleanup goal is not reasonably attainable. Monitoring with contingencies allows decisions and remedies to proceed, even in cases of high uncertainty.

A basic guiding principle for risk-informed decision making is that actions taken using a risk-informed cleanup process should: (a) improve the situation (b) not foreclose future options, and (c) minimize societal strain. A more detailed discussion of risk-informed decision making and approaches to assessing ecological risk can be found in Appendices B and C.

2.3. Comparison of DoD and Private/Commercial LUFT Sites

The characteristics of the ten DoD facility sites in the DoD LUFT Cleanup Demonstration Program spanned a wide range of hydrogeologic and petroleum release conditions and issues, and were generally representative of DoD LUFT sites in California. Appendix D summarizes key characteristics of the demonstration sites, with emphasis on those factors that impacted the Expert Committee risk-informed recommendations. Some of the DoD demonstration sites were in fact service stations located on DoD facilities; however, others involved much larger fuel storage and dispensing operations. As a result, experiences and strategies appropriate for typical service station sites may not be appropriate for all DoD sites in general.

According to U.S. EPA, the majority of petroleum cleanup sites across the United States are associated with gasoline releases from underground storage tanks (USTs) at service stations. Consequently, much of our experience with petroleum cleanups originates from these sites. Estimates of the quantities released are typically less than 10,000 gallons, most service station sites are less than 150 ft by 150 ft in area, and soils containing residual hydrocarbons do not extend far off-site, if at all.

Typical private/commercial LUFT sites are gasoline service stations that house 3 to 6 USTs on an area roughly 100 ft by 100 ft in size. When compared to these typical private/commercial LUFT sites, the Expert Committee found some characteristics of the DoD demonstration sites to be unique and critical to the risk-based decision-making process. These characteristics included the following:

- DoD LUFT sites generally occupy small portions of much larger DoD facilities,
- The types of DoD releases encompass a wider range of petroleum products than at typical UST release sites (e.g., light jet fuels -> gasoline -> heavy bunker fuels); although, in many cases only a single fuel type is stored at any given DoD LUFT site.
- The volumes of petroleum products transported, stored, and dispensed over time can be much larger than at typical non-DoD UST sites; therefore, quantities of petroleum liquids released can be very large in comparison with typical UST release sites, even when the site is a service station located on a DoD facility.
- Off-site properties are not always affected by the petroleum release, as is the case for most non-DoD petroleum release sites.
- At operating DoD facilities it may be easier to implement land use restrictions (often associated with natural attenuation corrective action plans) than at typical UST petroleum release sites.
- During the time period that corrective action decisions are being made, future land use may be uncertain at facilities that are, or will be closed; however, it is common for land use restrictions to be in place at the time of property transfer.
- There is typically much more public participation and oversight for cleanups at DoD facilities that at typical UST sites.
- The lead regulatory agency is not always the same agency that would typically oversee commercial/private UST cleanups in the area.
- Cleanup costs at DoD petroleum release sites can exceed the costs for typical UST site cleanup by at least an order of magnitude.

The DoD LUFT Cleanup Demonstration Program sites that were comparable to non-DoD LUFT gas stations were Camp Pendleton MCB Area 43 Gas Station Site, China Lake NAWS Exchange Gas Station Site, El Toro MCAS Site 390, Port Hueneme NCBC NEX Service Station, Presidio at San Francisco Building 637 Area, Travis AFB North/South Gas Stations, and Vandenberg AFB Exchange Gas Station Site (see Appendix D). Of these seven sites, all involved benzene releases, three had benzene plumes longer than about 400 ft, and five had MTBE plumes present. Of the MTBE plumes, two were longer than the benzene plumes, one being longer than

4,000 ft compared to a 1,000 ft benzene plume. The El Toro MCAS Site 390 Site was a soils only case and the release did not impact groundwater.

Among the remaining three sites, George AFB OU#2 and Castle Airport POL Fuel Farm Area, both represent releases of petroleum products associated with the transportation, storage, and dispensing of a wide range of petroleum products over time and the potential quantities of petroleum liquids released are large in comparison with typical UST release sites. The final site, the Barstow MCLC Tank 325 Site, was a diesel release associated with a sewage treatment facility.

Four of the ten sites had approximate estimates of the quantity of hydrocarbons released, while the remaining sites were unable to estimate the quantity released. The estimated quantity released ranged from about 2,300 gallons at the Vandenberg AFB Exchange Gas Station to 350,000 gallons at George AFB OU#2.

2.4. Conceptual Model for Fuel Hydrocarbon Releases

The idealized conceptual model of a dissolved fuel hydrocarbon groundwater plume consists of two essential elements. The first element is the residual hydrocarbon material that provides mass to the dissolved hydrocarbon plume. The residual hydrocarbons can be characterized by light non-aqueous phase liquids (LNAPL) either as free-product lenses floating on the capillary fringe, or as discrete ganglia entrapped within the vadose zone or even below the water table. The second element is the dissolved plume extending downgradient of the residual hydrocarbon area which is affected by advective and dispersive transport, retardation, and passive biodegradation. Natural attenuation processes, particularly passive biodegradation, may limit the downgradient migration of the dissolved plume (Grbic-Galic and Vogel, 1991; Cozzarelli et al, 1994; Hess et al., 1996; Kazumi et al., 1997). The interplay of the two elements leads to the concept of a steady-state plume existing under dynamic equilibrium conditions, where the mass influx of dissolved contaminants from residual free product is balanced by mass loss via passive biodegradation, integrated across the spatial extent of the plume. As it expands from its initial inception, and as long as passive biodegradation processes remain active, this stabilization point will always be reached by dispersion and advection during the evolution of the plume.

The management of each of the processes associated with these two elements of the plume conceptual model will play different roles in the establishment and evaluation of site-specific remedial goals. These remedial goals may be functionally divided into two broad categories:

1. Control of risk to current existing downgradient receptors.
2. Reduction of contamination in the subsurface to some specified concentration with a timing that is protective of current and probable future receptors.

The assessment of a site's dynamic equilibrium conceptual model, its integration into the site-specific sources-pathways-receptors risk model, and the nature of the evidence available to assist in risk-informed decision-making are all tightly coupled with the delineation of remedial goals. The EC has found that it is often possible to assess the dynamic equilibrium model processes at a given site with the data at hand; risk to existing receptors is usually tied to the assessment of passive bioremediation to potentially limit plume movement (Remedial Goal No. 1). However, Remedial Goal No. 2 has eluded definitive analyses because the necessary data are often not available to predict residual hydrocarbon depletion rates (and will likely not be available for the large majority of private/commercial LUFT sites). The reasons behind these findings reflect the nature of the evidence concerning passive bioremediation processes and residual hydrocarbon attenuation rates (by natural and/or engineered means), respectively.

2.4.1. Passive Biodegradation: Lines of Evidence and Estimation of Rates

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. 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 biodegradation actively destroys fuel hydrocarbon mass in the subsurface, limiting the spatial extent of the groundwater plume in the short term while eventually remediating the contamination over longer time periods. In principle, two lines of evidence may be called upon to assess passive biodegradation activity: primary evidence and secondary evidence.

Primary Evidence

Primary evidence includes quantitative evaluation of plume stability (or plume shrinkage or collapse) based upon statistical analyses of trends in historical groundwater contaminant concentration data (Buscheck et al., 1996). Although primary evidence of plume stability or decline provides the strongest arguments to support a passive bioremediation hypothesis at a given site, such evidence may not be available because adequate historical groundwater monitoring may not exist. This has been the case with most of the sites included in the Demonstration Program. In these instances, short-term monitoring data providing secondary lines of evidence, in conjunction with modeling where appropriate, may support a hypothesis for the occurrence of passive bioremediation. Consequently, means for assessing the role of passive bioremediation in controlling risk by secondary lines of evidence were addressed by the Expert Committee.

Secondary Evidence

Because historical monitoring data at fuel hydrocarbon spill locations are typically sparse, variations in geochemical indicator parameters are often used as indirect evidence of biodegradation. These include concentrations of electron acceptors (O_2, NO_3^-, SO_4^{2-}), reduced redox reaction by-products (Fe^{2+}, Mn^{2+}, CH_4), as well as bicarbonate alkalinity, pH, and redox potential (E_h) (Chappelle, 1994; Borden et al., 1995; Vroblesky et al., 1996). However, background variability in a number of these parameters complicates the task of data interpretation, particularly in the case of small data sets. Correlation analyses and population means testing have been applied to geochemical indicator data at several of the Demonstration sites to identify which parameters are the most reliable indicators. The results of the analyses suggest that the most direct indicators of the local redox environment – Fe^{2+}, Mn^{2+}, CH_4, E_h – yield the most consistent evidence of hydrocarbon biodegradation. Indicators which rely largely on mass balance – O_2, NO_3^-, SO_4^{2-}, bicarbonate alkalinity – may be less robust. These findings, presented in detail in Appendix E, Section E-1, may provide guidance in both the collection and interpretation of groundwater monitoring data at hydrocarbon contamination sites in general. Application of Monte

Carlo analysis techniques to assess passive bioremediation signatures at the NSGS site at Travis Air Force Base is presented in detail in Appendix E, Section E-2.

The estimation of representative passive bioremediation rates of dissolved hydrocarbon plumes at a site, particularly in the absence of adequate historical monitoring data, is not a straightforward issue. Two techniques are commonly employed to estimate mean first-order biodegradation rates at LUFT sites where the source release history is not well known. One method involves exponential regression of measured concentrations as a function of distance downgradient from the source area along the longitudinal axis of the plume (Buscheck and Alcantar, 1995). This approach assumes one-dimensional solute transport model which accounts for the presence of a continuous boundary concentration and a uniform first-order degradation coefficient. It must be recognized that this type of analysis is easily subject to misinterpretation, particularly when few monitoring points are used. This is because the dispersive nature of solute transport can produce concentration profiles which closely resemble those associated with a degrading contaminant even in the absence of any transformation processes. An analysis of this problem is presented in Appendix E, Section E-3.

2.4.2. Residual Hydrocarbon Attenuation and Engineered Free-Product Recovery

The anticipated time-to-cleanup was a key issue at each of the sites. This issue is both a technical issue and a policy issue. From a technical perspective, estimating the time to cleanup requires a determination of residual hydrocarbon product mass and attenuation rate, both of which are exceedingly difficult to obtain. From a policy perspective, if cleanup within a specified time frame is a remedial goal, then reconciliation of the required time frame with physical laws of contaminant behavior must be addressed. The need for active residual hydrocarbon removal must be addressed on a site-by-site basis and must include practical considerations of economic and technical feasibility.

These points are not addressed directly in current policies. For example, "U.S. EPA expects groundwaters to be returned to beneficial uses whenever practicable within a time-frame that is reasonable, given the particular circumstances of the site" (40 CFR 300.430(a)(l)(ii)(F). California regulations (Title 23, Health and Safety Code, Section 2655) require that the party responsible for site remediation "shall remove free product to the maximum extent practicable, as determined by the local agency." The adjectives "practicable" and "reasonable" are not formally defined in this context.

Forecasting the time required for plume collapse requires estimating the time scale of residual hydrocarbon depletion. If plume dissipation or collapse within relatively short time frame (Remedial Goal No. 2) is chosen as the governing issue for site cleanup, then from a mathematical modeling viewpoint as well as a practical reality in the field, plume collapse necessarily requires that the dissolved phase input to the plume from residual hydrocarbons be reduced or eliminated. This can occur naturally through weathering of residual hydrocarbons with time or through active removal activities (e.g., excavation, free-product skimming).

For natural depletion of the residual hydrocarbons, this requires estimates of light non-aqueous phase liquid (LNAPL) dissolution rates into groundwater as well as volatilization rates into the vadose zone. For engineered residual hydrocarbon removal, this requires an estimate of mass removal rates as a function of time. In any event, an accurate estimate of residual LNAPL volume is also necessary. From a characterization viewpoint, much of this additional information is extremely difficult to obtain or to estimate accurately. As a result, the time scale required for plume collapse, by natural source weathering and/or engineered source removal, often cannot be predicted with enough confidence to satisfy stakeholders.

If the residual hydrocarbon attenuation rate holds the key to plume remediation within a "reasonable" time frame, then there is an obvious inclination to attempt to remove residual hydrocarbon product to accelerate the cleanup process beyond the rate provided by natural mechanisms (dissolution and volatilization, combined with passive bioremediation). Most RWQCBs require active remediation of residual free product to demonstrate that it is technically or economically unfeasible to achieve site-specific cleanup levels. Fate and transport models can be used to compliment the evaluation, but a purely analytical evaluation in support of an unfeasibility determination appears to be unacceptable to many of the local RWQCBs.

Typical residual hydrocarbon removal technologies at LUFT sites include free-product removal, soil vapor extraction, bioventing, and over-excavation. Several factors should be considered in the selection of residual hydrocarbon zone treatment technologies:

- If the remedial goal is only to ensure plume stabilization, and passive bioremediation is shown to be effectively limiting plume migration, then treatment of the residual hydrocarbon zone soils is irrelevant.
- If the remedial goal is one of plume collapse within a decade, then active residual hydrocarbon zone treatment will likely be required.
- Each active remedial technology has a practical limitation of effectiveness and so technologies must often be applied in a sequence, with passive bioremediation being the final step in the treatment train.
- The benefits of LNAPL removal via over-excavation were illustrated by the results of the historical analysis of California leaking underground fuel tank (LUFT) cases (Rice et al., 1995b). These results indicated that over-excavation of the residual hydrocarbon area at LUFT sites with shallow groundwater increased the probability of observing both low average benzene plume concentrations and a decrease in benzene plume concentrations with time.
- Conventional LNAPL free-product extraction has limited effectiveness beyond about 30% to 50% of the original product mass. Conventional skimming may recover as much as 30%, high vacuum as much as 50%, and steam flooding as much as 90% of the original product mass (Beckett and Lendegard, 1997).
- LNAPL recovery efforts are especially difficult in cases characterized by low free-product thickness or relatively fine-grained soils.
- LNAPL extraction efforts are self-limiting in effectiveness. Recovery decreases with time because the removal of the most mobile portion of the LNAPL phase reduces the mobility of the remaining material. This occurs when capillary forces exceed the driving forces associated with the LNAPL gradient. Termination of actively engineered removal of free or residual product may be appropriate when the mass removal rate either reaches asymptotic levels or declines to levels where only *de minimus* amounts of product are being removed.

Alternative product removal technologies, such as high vacuum extraction or steam injection, should be evaluated in those situations where such high cost is warranted.

- Decision-makers should carefully weigh the benefits and costs of active remediation, and should recognize that active remediation systems by themselves rarely achieve drinking water standards in short time frames at groundwater-impacted sites.
- The main benefit of active remediation at most LUFT sites is not a reduction in risk of adverse impacts (because the maximum impact has usually occurred before it is observed), but is instead a reduction in time frame over which restoration of the site occurs.

2.4.3. Uncertainty and Data Analysis Approaches

In a broad context, several factors will determine the spatial extent of an ideal dissolved hydrocarbon plume emanating from a release area. These include mean groundwater velocity, the dispersion coefficients (reflecting the heterogeneous nature of the subsurface and the presence of preferential channels or pathways), the mean biodegradation rate, the conditions controlling dissolution of mass into the plume (e.g., rate of mass introduction, residual hydrocarbon area spatial extent and concentration, attenuation rate), the retardation coefficient, the porosity, and the aquifer vertical thickness. To assess risk to existing receptors, analytical or numerical models can be used to predict plume length as a function of time, assuming that representative values of governing parameters can be identified with sufficient accuracy. However, uncertainties concerning each of key parameters will translate into uncertainties in model forecasts. Recognizing this limitation, probabilistic modeling approaches have been employed as part of the Demonstration Program as a means of illustrating the uncertainties associated with plume evolution modeling and for identifying which factors exert the greatest influence on forecast values.

Petroleum hydrocarbon plume behavior uncertainty can be addressed by bounding estimates and then comparing predicted outcomes to observed behavior. The use of shared historical data is important to developing bounding estimates. The modeling approaches have involved two-dimensional analytical solutions to the solute transport equation with first-order degradation (with first-order source depletion in some cases) used in conjunction with Monte Carlo simulation to attempt to reproduce the observed statistical behavior of DoD Demonstration Program site hydrocarbon plumes. Probability distributions of governing parameters, such as hydraulic conductivity and passive bioremediation rates, were assigned based upon site data or best professional judgment and forecast distributions of plume length were generated.

Probabilistic plume behavior forecasts generally were in good agreement with the field observations (see Appendix E, Sections E-2 and E-4 for further results and discussion). Sensitivity analyses of forecast variance and uncertainty in governing parameters suggest that variance in plume lengths are affected primarily by uncertainty in hydraulic conductivity and the passive bioremediation rate.

2.5. Residual Risk Management Issues

The EC deliberations encompassed a wide range of issues that the EC members felt were pertinent to proper application of risk-based and risk-informed decision-making. Several of these issues could not be resolved, or their significance could not be assessed, primarily due to a lack of empirical data and a limited understanding of the underlying processes. In this section, we briefly summarize these issues and recommend that DoD and/or state regulatory agencies address these in the near future.

First, the EC recognizes that there may be adverse impacts caused by the by-products of natural processes occurring in the subsurface. Even with simple petroleum hydrocarbons, if residual petroleum hydrocarbons are left in the vadose zone or groundwater, the potential exists for sites to become anaerobic. If this is the case, methane could be produced from degradation of the hydrocarbons. When the methane production rate is high enough, the potential exists for gas-phase concentrations to build up and to exceed the lower explosive limit (LEL), and in some cases, the upper explosive limit (UEL). Similarly, as anaerobic conditions proceed in the subsurface, a potential exists for generation of hydrogen sulfide gas which may reach levels of objectionable olfactory levels. While neither of these extreme conditions were observed at any of the sites within the DoD LUFT Cleanup Demonstration Program, LUFT risk managers should be aware of their possible occurrence.

Second, some of the more likely exposure scenarios are not being routinely assessed or considered in current risk-based evaluations. For example, inhalation exposures during construction and excavation activities are a very real possibility at sites where residual hydrocarbons are left in place.

Third, it became clear that failure of tanks and pipelines at some of the sites was at least in part attributed to ground motion, (i.e., earthquakes, heavy railroad traffic). Therefore, consideration needs to be given to potential ground motion impacts to determine whether tank and piping at facilities may be vulnerable and warrant further evaluation. The threat of earthquakes in California is recognized, however, no strategy currently exists to determine where, when, and how tanks and piping should be evaluated following seismic events.

3. Findings

3.1. Risk-Informed Cleanup at DoD LUFT Cleanup Demonstration Program Sites

While alternative site-specific cleanup standards are not routinely allowed within California's regulatory frame work, risk-informed decisions are routinely made by regulatory staff. These decisions include acceptable time for cleanup, and how much data is required before no-further-action is permitted at DoD LUFT sites. Regional boards are able to issue no-further-action letters to responsible parties before reaching MCLs or background. The decision to issue a no-further-action letter or require further active remediation is typically made based on an evaluation of the time-frame for anticipated beneficial use and a balance between practical and economic considerations. No-further-action may be permitted in DoD LUFT cases where there are no risks to human health or the environment, and where passive bioremediation has shown to be destroying hydrocarbons at a rate sufficient to reach MCLs or background prior to anticipated beneficial use, and institutional controls exist to prevent exposure during the time passive remediation is occurring.

For those issues that regulators may use their own discretion to decide, e.g., an acceptable remediation time-frame or when a no-further-action letter may be issued, it appears that there is no clear state guidance. Moreover, there is a broad application of MUN to groundwater, even if the groundwater is unlikely to be used. This broad designation of MUN to groundwaters gives regulators the flexibility of requiring strict cleanup numeric goals and then relaxing active cleanup requirements when regulatory staff find the uncertainty in achieving the cleanup goals acceptable. This naturally leads to inconsistent decision making across a range of sites where a variety of case workers are involved, each with different interpretations of what may be acceptable in similar circumstances and other irrelevant factors may affect the decision making, e.g., perceived ability of a responsible party to pay for cleanup.

Although inconsistencies are often observed, DoD site managers typically do not want to appeal requirements that they believe to be inconsistent, unreasonable, or impractical because they do not want to damage relationships with site regulatory personnel ("Win the battle and loose the War" concerns). Further, DoD also wants to appear as a "good neighbor" and often has the resources to clean to strict standards, especially at closing military bases. For these reasons, the option of appealing inconsistent, unreasonable, or impractical requirements is very seldom exercised.

3.2. Site Conceptual Models

3.2.1. Conceptual Model Elements

The development of a site-specific conceptual model is a critical component in risk-informed cleanup. A conceptual model is made up of a series of hypotheses that guide characterization. A well defined conceptual model of a site contains sufficient information to: (1) identify sources of the contamination, (2) determine the nature and extent of the contamination, (3) identify the dominant fate and transport characteristics of the site, (4) specify potential exposure pathways, and (5) identify potential receptors that may be impacted by the contamination. Regional and local shared historical data can be used to develop site conceptual model hypothesis, particularly with regard to the fate and transport characteristics of the site.

In general, DoD LUFT site conceptual models were often not as well formulated as the EC had expected. The Expert Committee observed that during site briefings, a clear set of hypothesis regarding the nature and extent of the release and the factors that control the released petroleum hydrocarbon movement was often not provided or could be improved. Further, conceptual models were often recreated with each new contractor.

ASTM E1739-95, *Standard Guide for Risk-Based Corrective Action Applied at Petroleum Release Sites*, outlines guidelines for site characterization requirements. In general, the goal is to collect sufficient data to be able to classify a site, select an appropriate initial response action, and at a minimum conduct a Tier 1 analysis. Specific site characterization activities need to provide answers to the following questions:

(a) Are any known or suspected releases noted in the historical records?

(b) What sources of petroleum hydrocarbons have been, or are currently, present?

(c) What chemicals of concern (COCs) are present?

(d) What are the locations and values of maximum COC concentrations in soil and groundwater?

(e) Who or what could be impacted by the release?

(f) At what rate and to what extent have chemicals migrated to potential receptors?

(g) What are the current and future uses of the site and any impacted resources?

(h) What are the local and regional hydrogeologic conditions (if groundwater is, or is likely to be, impacted)?

When sufficient historical data are available, then the following can be ascertained:

(i) Has the extent of impact above levels of concern changed with time (i.e., is the plume growing, shrinking, or apparently stable?), and,

(j) Are the COC concentrations changing over time?

After answering these questions, a site conceptual model can be formulated and used for the basis of future decision making.

Experience gained from the DoD demonstration sites suggests that in many cases the existing data may be adequate to address (a) through (h), but not (i) and (j); however, temporal data are often lacking. In the absence of such data, evidence of ongoing biodegradation can be found in the secondary lines of evidence discussed above.

3.2.2. Summary of DoD LUFT Cleanup Demonstration Program Sites

Appendix C provides a brief summary of release conditions, risk management issues, and Expert Committee recommendations at each site in the DoD LUFT Cleanup Demonstration Program.

3.2.3. Management of Residual Hydrocarbons at DoD LUFT Cleanup Demonstration Program Sites

The application of risk-informed decision making can be illustrated through the consideration of the free-product removal at the DoD LUFT Cleanup demonstration sites. During risk-informed decision making, risk is considered in balance with economic and technical factors as well as stakeholder values. Actions taken should improve the situation, not foreclose future options, and minimize societal strain. In the context of California's current regulatory framework, required groundwater cleanup goals are to eventually reach background petroleum hydrocarbon concentrations in soils and groundwater. No-further-action may be allowed at a site when there is (1) a reasonable assurance that there are no current impacts to receptors, (2) background concentrations will be reached in the time frame commensurate with the probable anticipated future use of the resource, and (3) institutional controls exist to prevent exposure during the time passive remediation is occurring.

Among the DoD LUFT Cleanup demonstration sites, there were no human receptors that are currently impacted and risk evaluations focused primarily on the possibility for potential future exposure. The assessment of future risks at the demonstration sites is closely tied to the anticipated future land use at the site and probable beneficial use of groundwater resources beneath the site.

The EC members do not represent all the stakeholders involved in the cleanup decisions at each of the DoD Demonstration program sites, and while the EC has tried to solicit and consider values of each site's stakeholders, the EC's recommendations may or may not be used to make the actual cleanup decisions at a given Demonstration Program site. The following discussion poses the residual hydrocarbon management decision in view of site-specific tradeoffs to be weighed by stakeholders and as much as possible represents the consensus values of the EC members.

George Air Force Base

Among the Demonstration sites evaluated in this study, the Operable Unit (OU) #2 area at George Air Force Base (AFB) features a significant residual hydrocarbon mass, with an estimated 300,000 gallons of JP-4 aviation fuel present in the subsurface (McNab et al., 1997a). The dissolved benzene plume appears to be stable at a distance of about 1,200 feet from the area of residual hydrocarbon saturation, a stable dissolved petroleum hydrocarbon plume (TPH-g) plume extends 2,000 ft, and there is evidence that passive bioremediation is limiting overall plume migration. George AFB is a closing base which will be reused as the Southern California International Airport (SCIA). It is anticipated that existing building and facilities will also be used to support small business and light industry activities.

Much of the evaluation of risk management issues at the George AFB OU #2 center on the issue of continued operation of the existing free-product extraction system, reducing the uncertainty in risks to future receptors, and the acceptable conditions that may lead to no-further-action at the site. From a risk-informed perspective, the key uncertainties are related to plume stability and the time to reach background soil and groundwater concentrations. The uncertainties in plume stability has been reduced through the use of downgradient sentinel wells and contingency plans. Given our current limited understanding of vadose zone transport models and the depletion mechanisms of residual separate-phase hydrocarbons, it is not clear what measurements could be performed to reduce uncertainty in the estimate of residual hydrocarbon longevity.

If the acceptable conditions for no further action were to be defined as achieving plume stability to protect existing risk receptors, then free-product removal would not be warranted at the site because (1) passive bioremediation processes are limiting plume migration at the site, and (2) the nearest receptors are several miles downgradient. On the other hand, if dissolved plume dissipation or collapse within a short time frame is the remedial goal, then removal of the residual hydrocarbons contributing mass input into the dissolved plume would be needed. Free product is currently being removed from the aquifer by product skimming operations; however, at best this will only remove 30% to 50% of the initial residual hydrocarbons. Consequently, free-product recovery will not affect the dissolved plume extent in the foreseeable future. Thus, even with free-product recovery, one is faced with the daunting task of finding another cost-effective follow-up technology to treat the several acres of residual hydrocarbon containing aquifer and capillary fringe soils located approximately 100 ft below ground surface. The remaining residual hydrocarbons and the dissolved plume will likely persist for decades.

The George Air Force site presents an interesting dilemma. If there is no practicable follow-up remediation approach to free-product recovery at this site, is there any tangible benefit gained from any additional free-product recovery? Clearly, the free-product recovery itself would do little in terms of risk reduction as the aquifer has already been impacted to the maximum extent, the plume is stabilized, and there is no current or projected future use of the aquifer. Remediation costs in this type of setting for any available technology would be in excess of tens of millions of dollars.

In making a decision to continue free-product removal beyond the existing well skimming operations, risk-informed decision making differs from risk-based corrective action. Risk-based corrective action places a major emphasis on public health risk. While also considering public and ecological risk, risk-informed decision making considers stakeholder values which may not be quantifiable and are related to the perception of risk.

The anticipated time frame to reach cleanup goals is well beyond the normal short-term land use or water use planning horizon. Because of this, the Lahontan Regional Water Quality Control Board expressed concerns that these time frames exceed a reasonable planning horizon of about fifty years and wants active remediation of the residual hydrocarbons in the vadose zone to reduce risk to future potential users of the impacted groundwater. However, the lack of success in several vadose zone removal demonstration projects has not provided a functional cost effective solution.

While there is a perceived uncertainty in the effectiveness of long term institutional controls and long term land use, the layering of institutional controls at this site are significant. The institutional controls available include deed restrictions, requirements in the land transfer mandating it stay as an airport and the permitting requirements necessary to drill a well. In addition, the SCIA National Environmental Policy Act (NEPA) Environmental Impact Statement (EIS) and the reuse plan show the use of this property to remain airport runway and apron. In this situation, the trade off is between reducing the uncertainty in risk to future receptors to a degree that is not measurable or predictable versus the cost of attempting to remove free product from the vadose zone. It is the EC's value judgment that best management practices provide practical approaches to reasonably manage future risk. Both the U.S. EPA and California SWRCB policies require free-product removal to the extent practicable. The EC agrees that a general best management practice for free product is to remove that mass that is relatively easy to extract. The current active engineered extraction of 2,000 or more gallons of free product per month from the aquifer should continue until removal efficiency begins to substantially decline. Termination of actively engineered removal of free or residual product may be appropriate when the mass removal rate either reaches asymptotic levels or declines to levels where only *de minimus* amounts of product are being removed. After this point, use of low-cost natural processes, such as barometric pumping, to enhance the residual hydrocarbon weathering can produce significant, cost-effective benefits.

China Lake Naval Weapons Station

At the China Lake NAWS, an uncapped pressurized fuel line discharged an unknown quantity of gasoline for about 25 years (Kavanaugh et al., 1998b). While no free product has been observed, significant residual gasoline fuel hydrocarbons (FHCs) remain downgradient from the Navy Exchange Gas Station site, extending over 1,600 feet from the point of primary release. Recent groundwater data show that these residual hydrocarbons continue to contribute benzene, ethyl benzene, toluene and xylene (BETX), including MTBE, to the groundwater. The distal areas of the benzene and MTBE plumes do not overlap and the benzene plume appears to continue to move in response to a changing hydraulic gradient. A soil vapor extraction system has been installed at the site, but is not currently operating.

Despite the presence of these residual FHCs, risks to human health and the environment are minimal at this site. At the NEX site at China Lake NAWS, a baseline human health risk assessment has shown that risks are below regulatory concerns, based on reasonable exposure scenarios, and conservative exposure concentrations, and exposure assumptions. Because of the relatively poor water quality, there are no future plans to use the shallow groundwater impacted by the FHCs. Key future use uncertainties center on potential impacts to the deeper high quality regional aquifer.

A risk-informed approach would indicate that once indications of plume stability are evident, then a risk management strategy using monitored natural attenuation would be appropriate. As part of this approach, key monitoring points would be used to indicate any threat to deeper regional aquifers. Active remediation would be triggered if a threat to deeper aquifers is indicated.

Barstow Marine Corps Logistic Base

Among the other Demonstration sites where free-product extraction is not presently warranted is the Tank 325 site at Nebo Annex of the Marine Corps Logistic Base, Barstow, California (Pelmulder et al., 1998). Tank 325 supplied diesel fuel for a base sewage treatment plant. An estimated 18,000 to 23,000 gallons of diesel fuel were released over an unknown period. The site is near the Mojave River and the typical depth to groundwater is about 30 ft, although the water table elevation will fluctuate over a range of several ft during recharge events in the river. These fluctuations in the water table have made the separate-phase diesel less mobile by smearing the diesel across several feet of the vadose zone. Presently, less than one inch of free product is observed in two monitor wells near the release area.

The current groundwater plume does not threaten any existing drinking water wells and since the plume is beneath the sewage treatment percolation ponds and there are no anticipated plans for using this groundwater for drinking in the future, a long cleanup time is reasonable. There is evidence of passive biodegradation of the diesel and as the diesel weathers, lighter fractions evaporate and the potential for the remaining components to leach into the groundwater decreases with time. A key uncertainty is plume stability. Monitoring will be needed to reduce this uncertainty. If the plume is demonstrated to be stable, then active remediation of the residual diesel hydrocarbons is not warranted.

Vandenberg Air Force Base (AFB)

The Base Exchange Service Station (BXSS) at Vandenberg provides an illustration of the trade-offs between the uncertainty in potential risks and value and cost of additional information or active remediation (McNab et al, 1998b). During tank removal soil saturated and partially saturated with hydrocarbons was discovered in the area of the BXSS USTs. Over excavation was performed on soils showing signs of discoloration or residual hydrocarbon saturation. The site hydrogeologic and contaminant distribution conceptual model is well developed through 59 borings which sampled soils and groundwater. The impacted groundwater is a shallow seasonal perched aquifer in fine-grained clay sediments above a 400-ft Monterey shale unsaturated zone. The fractures in the Monterey shale are filled with clay minerals. Presently, there is minimal or absent free-product thickness and the fine-grained clay sediments limit any residual hydrocarbon mobility and recovery efforts. An MTBE plume has been detected at the site. Both the BETX and MTBE plumes appear to be stable. The groundwater capture zones of nearby Eucalyptus trees has been observed within both the BETX and MTBE plumes and are having a significant impact on the groundwater flow in the area.

The potential future use of the perched groundwater is very limited due to the uncertainties in continued anthropogenic recharge and the very low yields of the aquifer. The nearest drinking water sources are three miles up gradient in a deep regional aquifer that is below the extensive unsaturated zone. Thus it is reasonable to anticipate that the perched groundwater will likely never be used for beneficial use.

The key risk uncertainty is the possibility of downward migration of contaminated perched groundwater through the fractured Monterey shale to the regional aquifer. This uncertainty can be addressed two ways: (1) aggressively perform active remediation to eliminate the uncertainty of this threat, or (2) construct monitor wells within the Monterey shale in below the perched contaminated groundwater. There are technical limitations associated with active remediation. An extraction well field of 17 wells has been installed and the combined yield is about two gallons per day because of the restricted permeability of the clays at the site. Construction of deep monitor wells introduce new uncertain risks by potentially providing a transport pathway through the impermeable shale that may not have existed. The practical considerations and potential risks associated with these alternatives must be weighed in light of the degree of certainty in the site characterization and the assumption that contaminated perched groundwater will not migrate through the clay filled fractures in the shale. In this case, the EC agrees that it is very unlikely that mobile gasoline constituents, such as MTBE, will migrate through the 400-ft unsaturated zone during the time-frame that natural process will remediate the site.

Low-cost residual hydrocarbon remediation alternatives, such as passive soil vapor venting, phytoremediation, or curtailment of horticultural watering, and other perched aquifer recharge mechanisms, may provide the means for removing residual hydrocarbon material without incurring substantial operating costs or posing significant risks to potential future receptors.

Presidio at San Francisco

During the Loma Prieta earthquake, and possibly even earlier, an unknown volume of gasoline and diesel FHCs was released near the Building 637 area adjacent to Crissy Field (Small et al., 1998). The groundwater is 4 ft to 5 ft below the ground surface and salty organic rich marine sediments contribute to poor groundwater quality and little probability of future drinking water use. The Presidio has been turned over to the National Park Service and there is a desire to convert the military post into a national park. As such, land use restrictions may be inappropriate and aesthetic uncertainties play a significant role in the cleanup and risk management process. Extensive over excavation of the release area has removed any free product. Some residual hydrocarbons strongly sorbed onto the organic rich marine sediments may still exist.

The Presidio offers an illustration of the balancing of technical feasibility and aesthetic values. It is important to understand that there are technical feasibility limits to removing residual weathered petroleum hydrocarbons. Weathered petroleum hydrocarbons are typically depleted in volatile aromatic components and the remaining compounds are typically long-chain hydrocarbons. These long-chain hydrocarbons are relatively insoluble, immobile compared to the 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 which may be undesirable in the Crissy Field setting.

Fortunately these immobile long-chain hydrocarbons have much lower toxicity than the more mobile volatile aromatic components and they naturally degrade through microbial digestion and 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.

3.2.4. Recalcitrant Fuel Hydrocarbon Compounds

When making risk-informed decisions it is important to keep in mind that human and ecological toxicity data exists for only a handful of the hundreds of chemicals present in petroleum fuels. Thus, petroleum release risk management decisions and actions typically focus on only a few chemicals; those that have been identified as chemicals of concern primarily as a result of their toxicological properties and abundance in petroleum products.

The presence of the gasoline additive, methyl *tertiary* butyl ether (MTBE) at many UST sites in California has raised the possibility that other chemicals related to fuel hydrocarbons that pose a risk may be overlooked (Appendix F). Historically, as a matter of practicality, this risk and its uncertainty has been implicitly deemed to be acceptable. In moving forward with risk-based approaches, this uncertainty needs to be formally discussed, recognized, and accepted or rejected. Emphasis should be placed on assessing those chemicals that are both persistent and mobile in the environment. With respect to petroleum spills, the chemicals most worthy of scrutiny are fuel oxygenates, such as MTBE, and the monoaromatic compounds (e.g., trimethylbenzenes).

Recent surveys have shown that MTBE is present in the groundwater at over 90% of the leaking UST sites (Happel et al., 1998). MTBE was first added to gasoline as an octane enhancer in 1979, but did not become widely used in California until approximately 1994. California is one of eighteen states in the U.S. currently participating in the reformulated gasoline program, mandated by the requirements of the Clean Air Act Amendments of 1990. The composition of gasoline meeting these requirements must have either 2.0% or 2.7% oxygen in ozone or carbon monoxide non-attainment airsheds, respectively. MTBE, one of several oxygen containing compounds that could meet these requirements, may be present in gasoline up to a concentration of 15 percent by volume. See Appendix F for further information regarding MTBE.

At five of the ten DoD sites, Travis AFB (McNab et al., 1997b), Vandenberg AFB (McNab et al., 1998b), Port Hueneme (Everett et al, 1998), China Lake (Kavanaugh et al., 1998b), and Camp Pendleton (McNab et al., 1998a), MTBE was reportedly identified in the soil or groundwater. Reported maximum MTBE concentrations ranged from approximately 100 µg/L up to 30,000 µg/L, concentrations that are above the potential groundwater cleanup goals being considered. At four of the sites (Travis, Vandenberg, China Lake, and Camp Pendleton), the MTBE reported in monitor wells located within the current limits of the BTEX plumes. Because MTBE has the potential to migrate more rapidly in groundwater than the BTEX compounds, the observation of MTBE within the BTEX plumes suggests that releases of MTBE-free gasoline occurred prior to the release of reformulated gasoline at these sites. Among the sites, the most significant MTBE plumes (greater than 300 ft in length, as defined by the 20 ppb contour) exist at China Lake, Port Hueneme, and Vandenberg. However, each of the sites exhibits unique features which complicate the task of extrapolating the MTBE behavior and risk management strategies to other sites in general. For example, the MTBE plume at China Lake, on the order of 1,000 ft in length, occurs in a sparsely-populated desert environment and threatens no risk receptors. Groundwater along the anticipated flow path of the MTBE plume eventually discharges into a playa lake and there is a low probability of using the impacted groundwater.

At Port Hueneme, the MTBE plume, approximately 4,000 ft in length, appears to be confined to a high permeability channel, possibly a buried stream bed, through which it is migrating at a high velocity (approximately 0.5 to 1.0 ft/day). If the MTBE plume advance continues, the plume could eventually discharge into the surface waters of the port. An ecological risk evaluation of the potential MTBE impact to the port marine environment has yet to be performed. It may be expected that the impact of this particular plume to port ecosystems will be dwarfed by the impacts of port related hydrocarbon run-off and discharges, so the relative risk associated with the plume may not be high.

Finally, the MTBE plume at the Vandenberg AFB site resides within a shallow perched aquifer that exists as a result of anthropogenic recharge (lawn irrigation, runoff from a car wash operation); no existing receptors are threatened. As a result of this physical setting, future development of the perched zone for water supply purposes is not plausible, so again the risk associated with the MTBE plume is minimal.

3.2.4.1. Impact of MTBE on Remedy Selection

It is important to note that risk informed decision making is equally applicable to sites with and without MTBE present. The decisions regarding corrective action are, however, likely to be different at sites with and without MTBE. Knowledge of MTBE's chemical properties, fate and transport evaluations, site properties, and definition of possible pathways and receptors will lead to appropriate corrective action decisions.

Should active remediation of MTBE be required at a site, most of the existing remediation tools used to remediate BETX releases can successfully be applied to deal with MTBE. MTBE is only weakly retarded on soils, and in soils with organic carbon content less than 0.1%, MTBE will move at the same average rate as the ground water. In addition, MTBE appears to degrade at a rate significantly slower than benzene or the other aromatic compounds of concern at a fuel hydrocarbon release. Under some geochemical conditions, not yet fully understood, MTBE may not degrade at all. As a consequence, those sites that previously may have been potential candidates for application of monitored natural attenuation may no longer meet the necessary conditions for this remedy, if MTBE is present.

Pump and treat has been shown to be a viable option, because MTBE is only weakly adsorbed onto aquifer solids, and thus, fewer pore volumes are required to achieve cleanup levels, compared to benzene. Treatment costs are increased because MTBE removal from water is generally more expensive than benzene removal, although cost differentials may not be significant compared to transactional and capital costs for the site. Air sparging has also been successful in removing MTBE from the subsurface. Finally, reported successes using oxygen injection, or passive oxygen barriers, (oxygen releasing compound) indicate that engineered bioremediation may be applicable at some sites.

4. Recommendations and Discussion

Recommendation 4.1: Consistent guidance should be developed by the State of California to define target time frames for achieving remedial goals

State-wide guidance should consider current and future land use, as well as the implementability of relevant land-use restrictions. Target time frames should be set for both (1) ensuring contaminant stabilization (i.e., no further spreading/migration of contaminant), and (2) final closure of the site (i.e., achieving state-mandated target cleanup levels).

Recommendation 4.2: State-wide guidance is needed that formally recognizes that achieving low μg/L concentrations is not practicable in the short term (< 10 years) at most sites with groundwater impacted by fuel hydrocarbons

Definition of cleanup times must take into account basic constraints imposed by natural laws governing the transport and natural degradation process of petroleum hydrocarbons. The actual time required to reach groundwater cleanup goals are determined by these laws and limitations on residual hydrocarbon attenuation rates, through either active or passive processes, will practically constrain the time frame to achieve MCL cleanup goals. Guidance on the definition of what is reasonable and what is not technically or economically feasible would be an appropriate first step. Regional Water Quality Control Boards are encouraged to develop protocols for determining when active product removal efforts should be abandoned.

Additionally, recognition is needed that sites should be transitioned to remediation by natural processes at some point following implementation of active remediation options as appropriate. Guidance for determining the appropriate stage of corrective action for this transition is needed.

Recommendations 4.1 and 4.2 Discussion: The approach to reasonable or practical cleanup time requirements is not consistent between the seven regions that participated in the Demonstration Program, and the required time frame to meet numeric cleanup goals (MCLs/Background) are occasionally out of line with actual anticipated beneficial use, e.g., low yields or high TDS groundwaters. Risk-based decisions are allowed within California's regulatory framework with regard to setting the time frame for cleanup and no further action. Tied to the issue of protection of beneficial use, the "non-degradation" of groundwater resources, and no further action, is the question of when the resource is to be used.

Greater involvement of local water management agencies may be needed to decide reasonable time frames for anticipated beneficial use of groundwaters. As the physical and economic constraints on reaching MCLs or background in a relatively short time are more recognized and benefits of passive bioremediation utilized, the need for local determination of beneficial use of groundwater resources will likely increase.

It is important to note that for many groundwater contaminants, such as most petroleum hydrocarbons, natural degradation will reduce the risk associated with contaminant concentrations to acceptable levels. The key risk management issue in California DoD LUFT cases is the time frame for anticipated beneficial use.

For example, if a groundwater resource is currently being used for municipal supply and it is likely that impacted groundwater will enter the public drinking water supply, then this scenario is a high risk situation that requires immediate active remediation to cleanup goals that are protective. On the other hand, if the impacted groundwater is not now used for drinking water supply and the potential anticipated use is 30 to 50 years in the future, or never, then cleanup can take a longer period of time, possibly through natural processes. Regional Water Boards have the discretion to designate the time frame for anticipated probable beneficial use.

There is no "reasonable" upper limit for the time frame for cleanup. Key to the decision-making process is the anticipated time until the groundwater resource will probably be used. There are situations in which groundwater resources may have no probable beneficial use, thus extended time-frames for cleanup are acceptable. Important factors include: current water use, historical and future projections, land use controls, and plume behavior and control. 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.

In the past, the SWRCB/RWQCBs have viewed water resources as "receptors" not as only a pathway for contaminant transport. Any impacts to groundwater resources are *a priori* assumed to be unacceptable; while risk-based approaches more formally consider the likely use and value of the aquifer in the decision-making process.

Risk evaluations can be directed to any identified hazard. Risk based cleanup approaches can call for aquifers to be considered resources and for MCLs to be set as uniform cleanup levels, if that is how current policy is interpreted according to a regional value system. Aquifer cleanup time frames can be linked to generic beneficial use designations (e.g., potable, agriculture, no beneficial use, etc.). This would not require major changes to regulatory policy in most cases.

Existing policies/guidelines emphasize and encourage relatively rapid residual fuel hydrocarbon removal through engineered remediation, while risk-based approaches can allow for longer target time frames to achieve the same remediation goals; thus, long-term remediation options, such as remediation by natural attenuation becomes more "acceptable" under risk-based approaches. The Regional Boards have the discretion to define acceptable remedial time frames on a site-by-site basis, and to define appropriate interim management and monitoring strategies. Thus, target remediation time frames are typically based on considerations of risk.

Issues where consistency in practicality and reasonableness may be improved include:

1. Residual hydrocarbon and groundwater extraction impracticality. Natural physical laws governing contaminant transport often prevent meeting MCLs or background in relatively short time frames.
2. Time frame for anticipated beneficial use. When properly used, passive bioremediation can help manage risk and achieve remedial goals.

As stated, the key technical and policy challenge to the development of risk management strategies at the Demonstration sites is the issue of time-to-cleanup. Local regulatory agencies, the Regional Water Quality Control Boards, are empowered to define "reasonable" cleanup times based on such factors as basin plans and future anticipated land use. However, these factors alone do not take into account the hydrogeological and biogeochemical processes which ultimately govern the fate of the contamination problem. Specifically, certain key difficulties emerge in requiring cleanup times that do not consider governing natural processes:

- The dynamic equilibrium conceptual model suggests that the rate of residual petroleum hydrocarbon attenuation (either through natural or engineered means) is the principal variable controlling the rate of plume collapse and the ultimate realization of background cleanup goals. However, unlike other variables such as groundwater velocity or the passive bioremediation rate, the residual hydrocarbon attenuation rate is almost completely unconstrained upon examination of available data.
- In many instances, the ultimate benefit of engineered efforts at free-product removal in significantly reducing cleanup times is difficult to quantify because of a paucity of data. Moreover, even when a significant cleanup time benefit may be realized, the overall benefit to risk reduction may be relatively modest and not justify the costs incurred. As an example, consider a hypothetical situation in which "reasonable" cleanup time for a LUFT site is defined as 20 years. If natural attenuation processes alone would require 150 years to dissipate a plume below MCLs, and engineered residual free-product removal efforts were to reduce this number to 100 years, the overall cost-effectiveness of engineered removal may not warrant its use.

It must be recognized that natural attenuation processes (dissolution and volatilization of residual LNAPL, passive bioremediation of the dissolved FHCs) will eventually remediate the hydrocarbon contamination, over some time scale, without engineered assistance. In the meantime, the dynamic equilibrium conceptual model implies a likelihood of plume stability, which is consistent with the findings of the Demonstration programs as well as the observations of the LUFT historical case analysis (Rice et al., 1995b; Mace et al., 1997). Institutional controls provide an additional layer of protection from risk during the time period in which the plume's behavioral regime shifts from one of pseudo-stability to one of decline. The uncertainty associated with the implementation of institutional controls over long time frames is no more pronounced than the uncertainty associated with predictions of cleanup time under engineered residual LNAPL removal.

Thus, there is no real need for major regulatory framework changes. The basic ability to manage risk and preserve probable beneficial use of resources is already in place. Some different interpretation and implementation of existing regulations and policies is needed along with more local involvement of groundwater resource and land use planners. Consistency among DoD sites may be improved by greater utilization of the appeals process and a broader understanding of the natural constraints limiting cleanup processes.

With the increased use of risk-informed decision making for setting remedial goals and the use of monitored natural attenuation to meet remedial goals, it is possible that more residual hydrocarbons may be left in place at LUFT sites at the termination of active remedial action. These residual hydrocarbons will remain in soil and groundwater, slowly attenuating and degrading at sites across the country for years and potentially decades to come.

As a result, regulatory agencies may need to take a broader, regional view of LUFT site remediation, incorporating the presence of residual hydrocarbons (and other compounds too) into overall groundwater basin management. This should include an understanding of the long-term interactions between shallow and deep ground water, the potential influence of groundwater extraction on plume migration, the potential for vertical migration through conduits, and the connections between surface water and ground water. To help minimize exposure potential, this information on the location of residual hydrocarbons should be readily available to the public.

In addition, there is a need to develop institutional controls and land-use plans that consider the long-term management of residual petroleum hydrocarbons at individual sites throughout aquifer systems. These controls could be linked to the permitting process for activities that create the potential for exposure, such as soil excavation and water well drilling. There is a need to ensure the longevity of these controls by providing the institutions with funding and staffing for appropriate monitoring and enforcement.

Recommendation 4.3: DoD should develop and use a site conceptual model as the focal point of the corrective action decision-making process at each site

Each site identify a keeper of conceptual model. A commonly accessible data base should be established to promote shared historical case data and foster development of conceptual model hypotheses. Sites should share data to reduce uncertainty. The question of site characterization adequacy should always be linked back to the uncertainty in the site conceptual model.

Recommendation 4.3 Discussion: As a rule, subsurface fate and transport process and environments are complex and DoD LUFT cleanup risk management decisions are made with sparse data. The focus of site characterization should be to reduce the uncertainties in key decision-making parameters to support risk informed cleanup. The question of site characterization adequacy should be linked back to the site conceptual model hypothesis. The uncertainties in the conceptual model guide the characterization process.

Significant cost saving may be realized if the conceptual model for a given site is clearly stated and communicated to remediation contractors. This will focus their efforts and help minimize unnecessary characterization costs. Environmental decisions at the DoD LUFT Cleanup Demonstration Program sites are typically made with sparse data. Sites should share data to reduce characterization costs and uncertainty.

Recommendation 4.4: Better approaches for estimating residual petroleum hydrocarbon longevity are needed

As it will play an important role in risk-informed decision making, and since current approaches are inadequate, a national research priority should be to develop better approaches for estimating residual petroleum hydrocarbons longevity. Free product and residual hydrocarbon recovery should not be attempted beyond what can be reasonably expected given natural subsurface constraints upon the recovery process. As part of the National Test Site Program, DoD needs to do research to be able to better project source zone longevity under scenarios involving natural conditions, and partial remediation followed by natural attenuation.

Recommendation 4.4 Discussion: Residual hydrocarbon treatment/management should recognize that about 30 to 60% of FHCs reaching the water table can't be removed by free-product recovery only. Residual hydrocarbon management beyond free-product recovery should consider the following points:

- The probability of success in treating vadose zone residual hydrocarbons with active remediation is much higher than treating residual hydrocarbons trapped below the water table, given currently available technologies.
- Costs for treating contaminants trapped below the water table are greater by 2 to 5 times (ballpark guess) relative to vadose zone treatment.
- The most effective technology for treating residual hydrocarbons below the water table is either: (1) excavation of the impacted soils, or (2) de-watering followed by vadose zone technology treatment.
- In the absence of active remediation, submerged residual petroleum hydrocarbons are likely to remain for many decades or even centuries, depending on the magnitude of the release.
- Current risks to human health are insignificant at most sites, even in the absence of treatment, as the impacted groundwater is often not being used for potable purposes.

Given the technical issues associated with free-product extraction system performance over the long term, practicality may be most appropriately defined in terms of the impact on risk. This definition, in turn, draws again upon the selection of a remedial goal for a site. If the remedial goal is one of plume stabilization to protect existing downgradient receptors, free-product removal is essentially irrelevant as a remediation technology and is thus unreasonable by default.

If, on the other hand, the remedial goal is one of plume collapse in a relatively short time frame, then free-product extraction must be carefully evaluated in terms of long-term risk reduction. Residual hydrocarbon depletion models are a means of bracketing the uncertainties associated with time-to-cleanup estimates when the second category of remedial goals, plume collapse, is chosen as the appropriate remediation driver for a site.

Free product extraction will be practicable for this purpose only if certain conditions are met (e.g., shallow depth to groundwater, significant product thickness, coarse-grained material, small areal extent of product) which would favor over-excavation or yield appreciable recovery. Beyond the envelope of these conditions, the ultimate reduction in risk associated with shorter clean up times cannot be demonstrated. In such cases, free-product extraction may be deemed impracticable purely from a cost/benefit perspective.

5. References

American Society for Testing and Materials (ASTM) (1995), “Standard Guide for Risk-Based Corrective Action at Petroleum Release Sites,” E 1739-95.

Beckett, G. D., and P. Lundegard (1997), “Practically impractical –The limits of LNAPL recovery and relationship to risk,” in *Proceedings of the Petroleum Hydrocarbons and Organic Chemicals in Ground Water Prevention, Detection, and Remediation Conference*, Houston, Texas, November 12–14.

Borden, R. C., C. A. Gomez, and M. T. Becker (1995), “Geochemical Indicators of Intrinsic Bioremediation,” *Ground Water,* **33**(2), 180–189.

Buscheck, T. E., and C. M. Alcantar (1995), “Regressive techniques and analytical solutions to demonstrate intrinsic bioremediation,” in *Intrinsic Bioremediation,* R. E. Hinchee, J. T. Wilson, and D. Downey, Eds. (Battelle Press, Columbus, Ohio) pp. 109–116.

Buscheck, 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 12–15.

California Water Code Section 13000 "Porter-Cologne Act."

Chappelle, F. H., P. M. Bradley, D. R. Lovley, and D. A. Vroblesky (1996), "Measuring Rates of Biodegradation in a Contaminated Aquifer Using Field and Laboratory Methods," *Ground Water*, **34**(4), 691–698.

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.

Everett, L. G., S. J. Cullen, D. W. Rice, W. W. McNab, B. P. Dooher, M. C. Kavanaugh, P. C. Johnson, W. E. Kastenberg, and M. C. Small (1998), *Risk-Based Assessment of Appropriate Fuel Hydrocarbon Cleanup Strategies for the Naval Exchange Gasoline Station, Naval Construction Battalion Center, Port Hueneme, California*. Lawrence Livermore National Laboratory, Livermore, Calif. (UCRL-AR-130891).

Grbic-Galic, D., and T. M. Vogel (1987), Transformation of Toluene and Benzene by Mixed Methanogenic Cultures, *Applied and Environmental Microbiology*, **53**(2), 254-260.

Happel, A. M., E. H. Beckenbach, R. U. Halden (1998), *An Evaluation of MTBE Impacts to California Groundwater Resources*. Lawrence Livermore National Laboratory, Livermore, Calif. (UCRL-AR-130897).

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

Johnson, P. C., D. W. Rice, W. W. McNab, L. G. Everett, M. C. Kavanaugh, W. E. Kastenberg, M. C. Small, and S. J. Cullen (1998), *Risk-Based Assessment of Appropriate Fuel Hydrocarbon Cleanup Strategies for the Petroleum, Oils, and Lubricants Yard, Castle Airport, California*. Lawrence Livermore National Laboratory, Livermore, Calif. (UCRL-JC-131034).

Katsumada, P. T. and W. E. Kastenberg (1997), "On the impact of future land use assumptions on risk analysis for superfund sites," *J. Air and Waste Manage. Assoc.* **47**, 881–889.

Kavanaugh, M. C., D. W. Rice, W. W. McNab, M. C. Small, S. J. Cullen, P. C. Johnson, L. G. Everett, and W. E. Kastenberg (1998a), *Risk-Based Assessment of Appropriate Fuel Hydrocarbon Cleanup Strategies for Site 390, Marine Corps Air Station (MCAS) El Toro, California*. Lawrence Livermore National Laboratory, Livermore, Calif. (UCRL-AR-129151).

Kavanaugh, M. C., W. W. McNab, D. W. Rice, P. C. Johnson, M. C. Small, W. E. Kastenberg, L. G. Everett, and S. J. Cullen (1998b), *Risk-Based Assessment of Appropriate Fuel Hydrocarbon Cleanup Strategies for China Lake Naval Air Weapons Station, Navy Exchange Gas Station Site*, Lawrence Livermore National Laboratory, Livermore, Calif. (UCRL-AR-129578).

Kazumi, J., M. E. Caldwell, J. M. Suflita, D. R. Lovely, and L. Y. Young (1997), "Anaerobic Degradation of Benzene in Diverse Anoxic Environments," *Environmental Science and Technology*, **31**(3), 813–818.

Mace, R. E., C. I. Mayfield, and J. F. Baker (1997), *Extent, Mass, and Duration of Hydrocarbon Petroleum Storage Tank Sites in Texas*, Bureau of Economic Geology, University of Texas at Austin, Geological Circular 97-1.

McNab, W. W., B. P. Dooher, D. W. Rice, M. C. Kavanaugh, P. C. Johnson, S. J. Cullen, L. G. Everett, and W. E. Kastenberg (1997a), *Assessment of Appropriate Fuel Hydrocarbon Cleanup Strategies for George Air Force Base, Victorville, California, Using a Risk-Based Approach.* Lawrence Livermore National Laboratory, Livermore, Calif. (UCRL-AR-125619).

McNab, W. W., B. P. Dooher, D. W. Rice, M. C. Kavanaugh, S. J. Cullen, L. G. Everett, W. E. Kastenberg, M. C. Small, and P. C. Johnson (1997b), *Assessment of Appropriate Fuel Hydrocarbon Cleanup Strategies for Travis Air Force Base, Fairfield, California, Using a Risk-Based Approach.* Lawrence Livermore National Laboratory, Livermore, Calif. (UCRL-AR-125941).

McNab, W. W., D. W. Rice, S. J. Cullen, L. G. Everett, P. C. Johnson, W. E. Kastenberg, M. C. Kavanaugh, M. C. Small, and Tina M. Carlsen (1998a), *Risk-Based Assessment of Appropriate Fuel Hydrocarbon Cleanup Strategies for Area 43 MWR Gas Station, Marine Corps Base, Camp Pendleton, California.* Lawrence Livermore National Laboratory, Livermore, Calif. (UCRL-AR-128220).

McNab, W. W., B. P. Dooher, D. W. Rice, S. J. Cullen, L. G. Everett, M. C. Kavanaugh, W. E. Kastenberg, M. C. Small, and P. C. Johnson (1998b), *Risk-Based Assessment of Appropriate Fuel Hydrocarbon Cleanup Strategies for Base Exchange Gas Station Site, Vandenberg Air Force Base, California.* Lawrence Livermore National Laboratory, Livermore, Calif. (UCRL-AR-126774).

Pelmulder, S., W. W. McNab, Small, M. C., W. E. Kastenberg, D. W. Rice, M. C. Kavanaugh, P. C. Johnson, L. G. Everett, and S. J. Cullen (1998), *Risk-Based Assessment of Appropriate Fuel Hydrocarbon Cleanup Strategies for Tank 325 Site at Nebo Annex, Marine Corps Logistic Base, Barstow, California,* Lawrence Livermore National Laboratory, Livermore, Calif. (UCRL-AR-129579).

Rice, D. W., B. P. Dooher, S. J. Cullen, L. G. Everett, W. E. Kastenberg, R. D. Grose, and M. Marino (1995a), *Recommendations to Improve the Cleanup Process for California's Leaking Underground Fuel Tanks (LUFTs),* Lawrence Livermore National Laboratory, Livermore, Calif. (UCRL-AR-121762).

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 (1995b), *California Leaking Underground Fuel Tank (LUFT) Historical Case Analyses*, Lawrence Livermore National Laboratory, Livermore, Calif. (UCRL-AR-122207).

Small, M. C., W. W. McNab, D. W. Rice, S. J. Cullen, L. G. Everett, M. C. Kavanaugh, W. E. Kastenberg, and P. C. Johnson (1998), *Risk-Based Assessment of Appropriate Fuel Hydrocarbon Cleanup Strategies for Presidio at San Francisco, Building 637 Area.* Lawrence Livermore National Laboratory, Livermore, Calif. (UCRL-AR-129152).

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.

Appendix A

Development of Remedial Goals

Appendix A

Development of Remedial Goals

Matthew C. Small

The ultimate objective of establishing a remedial goal is to protect human health and the environment through risk reduction, exposure prevention, resource protection, and cleanup. Cleanup requirements or standards are set by states or the Federal Government to ensure that sufficient contamination is removed to protect human health and the environment. Under this broad umbrella of concerns, considerations such as groundwater use, aquifer beneficial use designation, cleanup costs versus risks, technical feasibility of cleanup, available expertise, available funding, permitting, anticipated land use, and property transfers may also play a role in setting these standards.

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

1. Analytic 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 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. If conditions at the site do not exceed remedial goals, the site will usually receive a status of "no further action required." However, if site conditions do exceed remedial goals, then several choices exist (Small, 1995):

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 impractical.

Cleanup to an overall or generic standard: This approach is also 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 or impractical 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.

Site specific risk-based objectives can take several forms. Site-specific, risk-based numeric soil and groundwater cleanup objectives can be developed. The American Society for Testing and Materials (ASTM) risk-based corrective action (RBCA) protocols give examples of this approach. Another approach is to use functional requirements, such as classifying exposure hazards (high vs. low risk sites) based on proximity to release location, and then setting cleanup objectives based on this classification.

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 component for setting remedial goals 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.

A-1. Selection of Remedial Goals at DoD Demonstration Sites

The remedial goal helps to establish the criteria for completing cleanup and achieving closure at the site. One of the key issues facing the DoD sites that were part of the LUFT Cleanup Demonstration Program was the fact that remedial goals were not clearly defined for the majority of sites in this study. This created a major difficulty because remedial goals drive all of the decisions regarding the corrective action process at a site. Without clear remedial goals, the implied goal is often assumed to be background or non-detect concentrations at all points within the plume. Cleanup then proceeds until the responsible party either complains or concentration reductions begin to show diminishing returns (i.e., the concentration versus time curve becomes asymptotic to some concentration). This is an inefficient way to address corrective action.

However, if remedial goals are established early on in the corrective action process, the responsible party can more intelligently and efficiently select strategies for achieving those goals. In addition, if remedial goals are determined through a risk-informed decision-making process, the corrective actions taken at the site can be targeted to achieve the maximum risk reduction.

The process of establishing remedial goals should involve all interested and affected parties to the extent possible. In practice, this process also involves a certain amount of negotiation to achieve the maximum benefits with the available resources. This negotiation process can be difficult and even contentious. In fact, the EC found that site staff were typically reluctant to contest or appeal what they felt to be unreasonable cleanup objectives.

A-2. Remedial Technology or Process Selection

- Remedial goals determine the amount of remediation needed, and the time frame or urgency for remediation. There may be several remedial alternatives or technologies which will achieve the remedial goals in the specified time frame.
- Remedy decision factors should balance cost versus time to achieve the cleanup goals.

- 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.

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

Remedy decision factors should balance cost versus time to achieve the cleanup goals. Active remediation typically occurs in a shorter time, at a greater cost, and may reduce the uncertainty in the time to cleanup. Passive bioremediation typically occurs in a longer time frame, at a lower cost, but there may be greater uncertainty in the time to cleanup. The technology or process should ideally perform this task as quickly, efficiently, and cost effectively as possible.

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. The monitored natural attenuation option, as with any remedial option, may be considered a viable remedial option if it is capable of meeting the established remedial goal within the allotted time frame while maintaining protection of receptors. However, this approach may require site-specific exposure and risk assessment, to determine threats and impacts to public health and the environment (Small, 1995). Additional consideration such as institutional control may be required to manage long-term exposure potential.

While remedial goals were typically not clearly established for the sites in the Demonstration program, it is possible to match some potential remedial technologies or processes with some likely 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 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 ground water. 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.

Plume status (i.e., shrinking, stable or expanding) may play a key role in the selection of remedial technologies. For shrinking and stable plumes, where sufficient containment has already been achieved, remedial technology selection will be determined mainly by concentration reduction and time frame considerations. In these cases, it is likely that monitored natural attenuation can be applied as a stand-alone option or as part of a combination of options to achieve remedial goals. For sites where residual petroleum hydrocarbons may remain in the subsurface for a long period of time, institutional controls or other long-term risk management strategies may also be appropriate.

However, for expanding plumes engineered approaches will generally be required to achieve containment or concentration based remedial goals. In these cases monitored natural attenuation will usually be appropriate only as a part of the remedial action or as a final step in the remedial process after engineered solutions have been completed. For any sites where receptors are impacted or threatened, engineered solutions will generally be required to reduce or prevent exposures.

References

Small, M. C. (1995), “Ex-Situ Corrective Action Technologies,” in *Proceedings of the 5th Annual UST/LUST Conference,* San Antonio, Texas, March 22, 1995.

Appendix B

Risk-Informed Decison Making

Appendix B

Risk-Informed Decision Making

William E. Kastenberg and Susan Pelmulder

Laws and public policy are implicitly or explicitly a statement of society's values. In an ideal democracy, federal, state, and local government codes reflect the values of the people, and the regulatory agencies enforce consistent adherence to these codes. Even if the codes and regulatory policies accurately represent consensus, individuals or groups of individuals may have different objectives or priorities and may disagree with the majority. Inclusion of all stakeholders in a transparent process builds confidence among the parties involved that a fair decision has been made.

One of the most difficult aspects of forming environmental policy is finding a balance between specificity and flexibility. Specific policies can provide detailed instructions for making remedial action decisions. For example, groundwater cleanup policies requiring background, non-detection or generic standards, such as drinking water standards, are very specific. In this case, the regulated conducts an investigation to determine the extent of contamination. When a regulator considers the site, the decision is already specified. If the contaminant levels are greater than the values specified in the water quality objectives, then action must be taken to try and meet the objective values. Deciding what action will best meet the water quality objectives is more difficult due to uncertainties in what lies below the ground surface, as well as technical difficulties in achieving some cleanup goals. This type of decision process can be applied uniformly across a wide variety of sites and is transparent, both of which contribute to the appearance of fairness. In summary, specificity is required to prevent arbitrary decisions or even the appearance of arbitrariness, since that goes against basic principles of fairness and justice.

The disadvantage of water standard based cleanup goals is that they are not very flexible. Flexibility is required to efficiently allocate often times limited financial and personnel resources to achieve the maximum benefit. In some cases, flexibility is also required for fairness. Sites where a rigid standard is applied, regardless of the land use or the people effected by the decision may not be considered fair. In introducing flexibility into cleanup policy the decision process becomes more complex, and possibly less efficient and less transparent than standards based decisions. This is the price for increased efficiency in the cleanup phase, as well as efficiency in overall cleanup of the State's waters. Cleanup goals incorporating site-specific risk assessments within a well defined framework can be both uniformly applied and flexible.

In California, the Porter-Cologne Act (CA WC Sec. 13000) states, "that the people of the state have a primary interest in the conservation, control, and utilization of the water resources of the state, and that the quality of all waters of the state shall be protected for use and enjoyment by the people of the state." A State Water Resources Control Board and nine California Regional Water Quality Control Boards (RWQCBs) were created to administer water policy and execute the protection of the state's waters. The regional boards were given the flexibility to interpret and implement policy, taking into consideration hydrogeology, meteorology, and water uses in their regions. Although subsequent policy written by the State and RWQCBs has not included a risk-informed decision process, such a decision process is consistent with the Porter-Cologne Act.

In its general definition, risk is the probability of an adverse event. The adverse event may be financial loss, human injury or death, loss of species, or degradation of resources. In even more general terms, the adverse event may be something difficult to quantify, like anxiety or reduction in quality of life. Furthermore, individuals have differing views on what events are adverse. To conduct risk evaluation and management at a site, it is first important to know what the stakeholders value. This is essential both for determining what risks to evaluate and for setting remedial goals. For many sites with small impact, the process of public hearings and a full risk assessment may be too costly and too time consuming to be useful. Hence, policy and risk evaluation methods are needed which streamline the evaluation and decision process. One of the advantages of a tiered approach, such as The American Society for Testing and Materials (ASTM) risk-based corrective action (RBCA), is that the analysis is only as detailed as is necessary to be reasonably certain that public, ecological and resource health are protected.

There have been a few recent publications describing different approaches for risk based decisions, such as in the National Research Council (1994 and 1996), The Presidential/Congressional Commission on Risk Assessment and Risk Management (1997), and ASTM RBCA. We do not intend to add yet another framework in this report; however, there are several insights we have found in attempting to use risk-based evaluations in remedial decisions. One is that basing decisions on a single risk number, or even a distribution of risk, can be as limiting to the decision process as previous methods. For this reason, we advocate a "risk-informed" decision process which evaluates risk in context of the physical and social surroundings of the site, as well as current regulations.

The U.S. Nuclear Regulatory Commission (1997a, b) has proposed a risk-informed decision making process for changes in nuclear plant licensing which has several features useful in environmental remedial action selection. This approach prescribes a protocol for both the regulator and the regulated. The regulated uses a combination of conventional engineering analysis and risk assessment in characterizing options and proposed choices. The regulator makes use of all available information to come to a decision, consistent with existing regulations, which meets risk goals, maintains safety margins, and addresses uncertainty.

As described in Appendix A, there are many possible risk goals and objectives in environmental remedy selection. From a practical standpoint, guidelines must be established for risk goals at the state and regional levels, rather than reinvented at every site. However, the guidelines should be flexible enough to incorporate site specific information and stakeholder concerns. Two important considerations in setting goals are land use and institutional controls

As explored in Katsumada and Kastenberg (1997), land use is an important consideration in determining current and future risk, and in selecting a remedy. For risk considerations, there are three basic land uses: commercial/industrial (which has restricted use), recreational (which has limited use), and residential (which has unrestricted use). Each of these land use categories result in different exposures and risks, and therefore different cleanup goals, for the same level of contamination. Higher risk values for residential areas result both from longer exposure times and from inclusion of more susceptible populations such as children.

Many sites with contaminated soils or groundwater are currently commercial/industrial. If it is assumed that they will continue to be commercial/industrial, then risk based cleanup goals will typically be less stringent than if it is assumed that the area will become residential. From a risk management standpoint, there are at least two ways of reducing the potential future risk of the site. One is to reduce the contaminant concentrations. The other is to use land-use planning, e.g., institutional controls, to prevent long exposures or exposure of susceptible populations. What use will be made of the land in the future is a function of both policy and individual choice. Policy may dictate that there are no restrictions on the land use but factors such as weather, infrastructure, and location may practically limit the use because business and residences may not want to locate there. Conversely, the land owner and local government may agree to a deed restriction to prevent excessive exposure and later be pressured into unrestricting the land use. Land-use planning can be an effective risk management tool, but requires consideration of the likelihood and time scale of future uses and the strength of particular institutional controls.

There are many sources of uncertainty in risk based decision making besides the future land use. Uncertainties in size and location of secondary sources, hydrogeology, geochemistry, and natural degradation processes all contribute to uncertainty in the magnitude and time-scale of future risk. Conservative assumptions in selecting models and their parameters are often used to address uncertainty. By compounding conservative assumptions, some safety margin is maintained, but its level is uncertain. Furthermore, with this approach efforts may be misdirected towards sites with large uncertainties, but with potentially low risks, instead of towards sites with better known, but potentially higher risks. To avoid compounding assumptions, mean values or best estimates of parameters should be used to calculate risk. In addition, the uncertainty should be estimated. A safety margin can then be established relative to the uncertainty and to the best estimate of risk.

In risk-informed decision making, monitoring is used to reduce uncertainty, both in the characterization of the site and in the likelihood that an inappropriate decision has been made. If the decision is to use a form of active remediation, such as groundwater pump and treat or soil vapor extraction, the performance of the design is generally monitored and progress of cleanup tracked. If the decision is to use natural attenuation, monitoring is used to confirm or improve the predicted attenuation rates. In either active or passive remediation, if new information indicates that the remedy will not achieve the cleanup goal, then both the remedy and the cleanup goal can be reconsidered. It may be that a different remedy is required, or it may be that the cleanup goal is not reasonably attainable. Decisions are usually made with incomplete and imperfect information. Monitoring with contingencies to reconsider, allow decisions and remedies to proceed, even in cases of high uncertainty.

In meeting risk goals, maintaining safety margins, and addressing uncertainty, there are three basic principles in selecting a remedy which stakeholders should try to achieve: (1) improve the situation, (2) don't foreclose future options, and (3) minimize societal strain. To improve the situation, the remedial action chosen should reduce the total risk. Because workers can be injured or exposed during cleanup activities, it is not always the case that doing more is better than doing less. If there is a high degree of uncertainty in either the geophysical or socioeconomic (e.g., future land use) aspects of the site, it is important to leave open the option to change the remedy in the future. For example, if the plume is young, it may not be known yet if the contaminant is degrading. A remedy may be selected on the assumption that the contaminant will degrade; however the remedy may need to be adjusted if new data shows that the degradation is not fast enough to prevent migration and exposure.

Clean water is an important resource, from economic and other social standpoints. Involving all of the stakeholders in the decision balancing costs (for example: economic, water resources, land use options, and aesthetics) with benefits derived from particular cleanup goals and remedy selections is necessary to minimize the overall impact on society. Considering a wider range of costs and benefits is consistent with the range of values of water stated in the Porter-Cologne Act (CA WC Sec. 13000): "beneficial and detrimental, economic and social, tangible and intangible."

In risk-informed decision making, cleanup goals relating to health and or socioeconomic risks are set with input from stakeholders representing both local and state concerns. A remedy is selected that balances costs with achieving cleanup goals and improves the situation. Uncertainty in both site characterization and the decision are addressed through monitoring with contingency plans.

References

Katsumada, P. T. and W. E. Kastenberg (1997), "On the impact of future land use assumptions on risk analysis for superfund sites," *J. Air and Waste Manage. Assoc.* **47**, 881–889.

National Research Council (1996), *Understanding Risk, Informing Decisions in a Democratic Society* (National Academy Press, Washington, D.C.).

National Research Council (1994), *Science and Judgment in Risk Assessment* (National Academy Press, Washington, D.C.).

U.S. Nuclear Regulatory Commission (1997a), "Framework for Environmental Health Risk Management," *The Presidential/Congressional Commission on Risk Assessment and Risk Management*, Final Report Vol. 1, Washington, D.C.

U.S. Nuclear Regulatory Commission (1997b), "Risk Assessment and Risk Management in Regulatory Decision-Making," *The Presidential/Congressional Commission on Risk Assessment and Risk Management*, Final Report Vol. 2, Washington, D.C.

Appendix C

Assessing Ecological Impacts

Appendix C

Assessing Ecological Impacts

Tina Carlsen

Determining the potential for ecological damage as a consequence of chemical releases into the environment is recognized as a critical component of the conceptual model (Suter and Loar, 1992**;** Carlsen, 1996). Indeed, several federal statutes (such as Comprehensive Environmental Response, Compensation and Liability Act, Resource Conservation and Recovery Act, and Federal Insecticide, Fungicide, and Rodenticide Act), require the identification and mitigation of ecological impacts associated with chemical releases into the environment. As a result, a variety of methods are available to estimate the ecological hazard from chemical releases. These methods range from the qualitative to quantitative (Solomon 1996, USEPA 1992; Warren-Hicks et al., 1989). Most of these methods share some basic elements. Typically, an evaluation of the potential pathways in which ecological receptors can be exposed to the chemical is conducted. The groups of exposed organisms are identified and the probable level of exposure determined. Finally, the ecological significance (if any) of this exposure is identified. While this last step is the most crucial, it is often the most difficult. While demonstrating exposure of an ecological receptor to a chemical is clearly necessary, it is not sufficient in determining if an ecologically meaningful impact has occurred.

When evaluating ecological exposure, it is necessary to identify or consider (1) the organisms that are actually or potentially exposed and the exposure level, (2) the significant routes of exposure, (3) the spatial and temporal scales of exposure, and (4) the geophysical, physical and chemical properties that could affect exposure. The exposure analysis will likely result in the identification of numerous species which could potentially be exposed to chemicals released into the environment. It is often necessary to group the biota into major ecological functional groups to simplify the initial exposure pathway analysis. Once the initial exposure pathway analysis is complete, specific groups of organisms may be selected for in-depth hazard assessment. Organisms selected for the detailed analysis are often considered “sentinel organisms” (Suter et al., 1987; Grizzle et al., 1988; Rice et al., 1994).

To determine the ecological significance of exposure to a chemical, it is necessary to select ecological endpoints to be examined. Endpoints are characteristics of an ecological component (such as fish mortality) that may be affected by exposure to a stressor (Suter, 1990; USEPA, 1992). It is useful to distinguish between two types of endpoints, assessment endpoints and measurement endpoints. Assessment endpoints are explicit expressions of the actual environmental values that are to be protected (USEPA, 1992; Warren-Hicks et al., 1989). Measurement endpoints are the measurable responses to a stressor that are related to the valued characteristics chosen as the assessment endpoint (Suter, 1990). In some cases, measurement endpoints and assessment endpoints are equivalent.

Although there are a number of ways to specifically define ecological assessment endpoints, in general they should (1) be relevant to society, (2) have biological or ecological relevance, (3) have an unambiguous operational definition, (4) be measurable or predictable, (5) be susceptible to hazard, and (6) be logically related to the policy or remedial decisions. In the context of evaluating the ecological impacts of petroleum hydrocarbon exposure, assessment endpoints should be environmental characteristics that if significantly affected would indicate the need for some type of action.

If endangered species are not involved, plants and animals are typically not valued biologically as individuals, and therefore the assessment endpoints are usually related to entire populations or communities (Warren-Hicks et al., 1989; Moriarty, 1983). An example of a population-based assessment endpoint would be "change in the abundance of aquatic or amphibian populations." However, due to their rarity, individual members of endangered species are considered essential to the survival of the species. In this case assessment endpoints related to individuals are appropriate. "Increase in mortality or decrease in reproductive potential of individual San Joaquin kit fox" is an example of an appropriate assessment endpoint in this case.

As mentioned above, measurement endpoints are a quantitative expression of an observed or measured effect of a stressor that is related to the valued characteristic chosen as the assessment endpoint. Measurement endpoints should have specific characteristics, depending on the problem at hand. Most importantly, measurement endpoints should (1) correspond to or be predictive of an assessment endpoint, (2) be readily measured, (3) be appropriate for the scale of the problem, (4) be appropriate to the exposure pathway, (5) be appropriate to temporal dynamics, (6) have low natural variability, and (7) be diagnostic of the contaminant of interest.

Continuing with the two examples given for assessment endpoints, corresponding measurement endpoints might include "reduced number of Least Bell's Viero eggs" and "fewer pups per litter for individual San Joaquin kit fox". These measurement endpoints clearly relate to the assessment endpoints. However, such measurement endpoints can require maintaining large lab populations for a significant length of time or conducting lengthy field studies. Recent research has focused on identifying biochemical changes which are precursors to reduced reproductive success. Examples include binding affinity to estrogen receptors and induction of the mixed-function oxidase enzyme system. However, care must be taken when using such biochemical measurement endpoints to show that they directly tie to the assessment endpoint.

References

Carlsen, T. M. (1996), "Ecological Risks to Fossorial Vertebrates from Volatile Organic Compounds in Soil," *Risk Analysis*, **16**(2), 211–219.

Grizzle, J., Horowitz, S. and Strength, D (1988), "Caged Fish as Monitors of Pollution: Effects of Chlorinated Effluent from a Wastewater Treatment Plant," *Water Res. Bull.* **24**, 951–959.

Moriarty, F. (1983), *Ecotoxicology: The Study of Pollutants in Ecosystems* (Academic Press, New York, N.Y.)

Rice, D. W., Seltenrich, C. P., Keller, M. L., Spies, R. B., and Felton, J. S. (1994), "Mixed-Function Oxidase-Specific Activity in Wild and Caged Speckled Sanddabs, *Citharichthys stigmaeus*, in Elkhorn Slough, Moss Landing Harbor and Nearshore Monterey Bay, California," *Environ. Pollut.* **84**, 179–188.

Solomon, K. R. (1996), "Overview of Recent Developments in Ecotoxicological Risk Assessment," *Risk Analysis*, **16**(5), 627-633.

Suter, G., Rosen, A., Linder, E., and Parkhurst, D. (1987), "End-points for Responses of Fish to Chronic Toxic Exposures," *Environ. Toxicol. Chem.* **6**, 793–809.

Suter II, G. W. (1990), "Endpoints for Regional Ecological Risk Assessment," *Environmental Management*, **14**(1), 19-23.

Suter, G. W., and J. M. Loar (1992), "Weighing the Ecological Risks of Hazardous Waste Sites: The Oak Ridge Case," *Environ. Sci. Technology*, **26**(3), 432–438.

U.S. Environmental Protection Agency (1992), *Framework for Ecological Risk Assessment*, U.S. Environmental Protection Agency, Washington, D.C. (EPA/630/R-92/001).

Warren-Hicks, W., Parkhurst, G. R., and Baker, S. S., Jr. (Eds.) (1989), *Ecological assessment of Hazardous Waste Sites: A Field and Laboratory Reference Document,* U. S. Environmental Protection Agency, Washington, D.C. (EPA/600/3-89/013).

Appendix D

Summary of Department of Defense Petroleum Hydrocarbon Cleanup Demonstration Program Sites

Table D-1. Summary of Department of Defense Petroleum Hydrocarbon Cleanup Program sites.

Site name	Hydrogeologic setting	Exposure: Primary source and residual hydrocarbons	Exposure: Potential pathways	Exposure: Potential receptors	Key issues	Risk assessment findings	Recommendations	References
Barstow Marine Corps Logistic Center Tank 325	**Mojave Desert alluvial setting: sands, gravels, silts, clay. No coherent bedding, extending hundreds of feet deep. Depth to water about 30 ft.**	**Leak from diesel UST as part of a waste water treatment plant. Approximately 20,000 gal diesel released. Residual free product in smear zone near surface of the water table.**	**Dissolved TPH-Diesel hydrocarbons extend about 600 ft downgradient. Plume relatively young. Off-site private well approximately one mile downgradient.**	**No existing receptors have been identified.**	**Where did 20,000 gallons of diesel go? What are seasonal changes in groundwater flow direction? How long will plume extend before it stabilizes? Is there any reasonable anticipated benefical use of groundwater?**	**Plume stability data not available. Plume is still young so it may still be growing. Facility will continue to be used as waste water treatment plant with associated sludge ponds. Secondary evidence of passive biodegradation of petroleum hydrocarbons. Strong biological activity in the subsurface environment due to waste treatment recharge.**	**• Additional monitoring point to verify plume stability. • Monitored natural attenuation. • Institutional controls to protect potential future receptors.**	**Pelmulder et al., 1998**
Camp Pendleton Marine Corps Base Area 43	**Unconsolidated fill and alluvium-sand, clayey silt. Depth to groundwater is 15 ft; clay aquitard about 4 ft thick. Creek is about 100 ft from release location; most likely is a gaining stream. Slow groundwater flow velocities—0.5 ft/day.**	**Former underground fuel tanks and piping at base service station. Unknown quantity of gasoline released. No residual hydrocarbons identified in soils.**	**Dissolved BTEX groundwater plume possibly truncated by nearby creek. MTBE detected in vicinity of UST locations. MTBE plume smaller than BTEX plume.**	**No existing human receptors have been identified. Potential to impact creek ecosystem and endangered bird: Least Bell's Vireo.**	**What are impacts to creek habitat and endangered bird?**	**Installation of monitoring wells in creek will be destructive of ecosystem. Stream sediment sampling indicate no BTEX compounds. Strong secondary evidence of passive bioremediation of BTEX compounds; Benzene likely to degrade before reaching creek. Endangered bird species is already part of base wide monitoring program. Aquitards prevent impact to regional aquifers.**	**• Additional monitoring to verify plume concentrations stability or decline. • Monitored natural attenuation with possible passive soil venting. • Institutional controls to protect potential future receptors.**	**McNab et al., 1998a**

Table D-1. (Continued)

Site name	Hydrogeologic setting	Exposure: Primary source and residual hydrocarbons	Exposure: Potential pathways	Exposure: Potential receptors	Key issues	Risk assessment findings	Recommendations	References
Castle Airport (Former Castle AFB) POL Yard	**Central Valley fluvial sediments; predominantly sands and silts. Fuel Farm is largely paved. Groundwater depth is 60 ft, but was as high as 20 ft bgs within last 50 yr. Groundwater velocity is high, about 3 ft/day.**	**Above ground storage tanks, underground storage tanks, rail head piping and pumping stations in operation since 1940's. Unknown quantities of diesel, gasoline, jet fuels released. Soil sampling indicates comparatively low concentrations of FHCs. Releases possibly small in volume or slow in rate; unusual for this type of facility. Soil gas data indicate explosive concentrations present over larger area than soil or groundwater data would indicate. No free product detected.**	**Two benzene plumes each less than 200 ft long.**	**No existing receptors have been identified.**	**What is the source of high concentration soil vapors? Closing base: base to be converted to public airport; future use of POL facility uncertain. What is the time frame for anticipated use of groundwater?**	**Dissolved BTEX and chlorinated solvent groundwater concentrations in excess of MCLs. Groundwater extraction system in place to cleanup nearby dissolved TCE groundwater plume will capture and treat any petroleum impacted groundwater.**	**• Determine integrity of existing above ground storage tanks and transfer lines. • Evaluate vadose zone treatment options of bioventing and soil vapor extraction.**	**Johnson et al., 1998**
China Lake Naval Weapons Center Navy Exchange Gas Station	**Mojave Desert alluvial setting. Clay aquitards underlies the site. Depth to water about 30 ft. High groundwater flow velocities, about 1 ft/day. Shallow groundwater of poor quality, >1,200 mg/L TDS.**	**Uncapped pressurized fuel line 1967–1993. Unknown quantity of gasoline released. Significant residual hydrocarbons extending about 1,100 ft from point of release. No free product currently observed, but groundwater TPH-g concentrations near solubility limit.**	**Soil gas and groundwater are the primary transport pathways. No ingestion pathway likely. Long benzene and MTBE plumes that are not stable, > 1,600 ft long. MTBE plume has migrated beyond BTEX plume.**	**No existing receptors have been identified. Receptors for possible inhalation impacts include residents, students, and workers. The aquifer will not likely be used for potable use due to high TDS (1,200 mg/L).**	**How long will plume extend before it stabilizes? What are vapor impacts to near by School? What is causing change in plume direction? Is there any reasonable anticipated beneficial use of the groundwater?**	**BTEX plume concentrations are declining. Secondary evidence of passive biodegradation of petroleum hydrocarbons. MTBE plume will stabilize through dispersion. No existing receptors have been identified; Inhalation pathway analyzed. Time to cleanup key technical issue. Aquitards prevent impact to regional aquifers.**	**• Install and additional monitoring well to define BTEX/MTBE plumes. • Additional monitoring to verify BTEX/MTBE plumes stability. • Active remediation to stabilize BTEX/MTBE plume migration, then monitored natural attenuation. • Institutional controls to protect potential future receptors.**	**Kavanaugh et al., 1998a**

Table D-1. (Continued)

Site name	Hydrogeologic setting	Exposure: Primary source and residual hydrocarbons	Exposure: Potential pathways	Exposure: Potential receptors	Key issues	Risk assessment findings	Recommendations	References
El Toro Marine Corps Air Station Tanks 390A/B	Alluvial fan deposits of silts and clays with interbedded sands and gravels. Depth to groundwater: 150 ft.	Former underground fuel tanks and piping at base service station. Unknown quantity of gasoline, diesel, and JP-4/JP-5 released at various times. Over excavation performed during tank removal. No free product observed. Minor concentrations of residual hydrocarbons in soils.	Soil samples indicate that fuel hydrocarbons have not migrated to the water table.	No existing receptors have been identified. Nearest down gradient agricultural well is two miles distant.	What are potential impacts to groundwater of the residual fuel hydrocarbons in the soil?	Deepest residual hydrocarbons in soils are at 110 ft. Groundwater monitor wells have been installed and no fuel hydrocarbons found.	• Prepare documents to request no further action at this site.	Kavanaugh et al., 1998b
George Air Force Base Operable Unit 2	Unconsolidated alluvium in arid climatic setting. Perched unconfined aquifer 125–200 ft below ground surface.	Leaks from former Aviation Fueling pits and piping system. Unknown quantity of aviation jet fuel released. Estimated 350,000 gal of separate phase JP-4 aviation fuel on perched aquifer. About 160 gal of free product per day removed (32,000 gal to date).	No existing receptors have been identified. Stable plume length. Dissolved benzene plume about 1,200 ft beyond margin of free product.	No existing receptors have been identified.	How long will source persist? What natural process are depleting the residual hydrocarbons? How much of the residual hydrocarbons can be removed? What are the hazards of the remaining residual hydrocarbons? Time to cleanup key technical issue; land use planning is uncertain beyond 50 yr.	Significant residual hydrocarbons will persist for decades. Free product recovery efforts will not likely be effective; estimate 30% free- product removal optimistic. Passive biodegradation is likely limiting dissolved hydrocarbon plume migration.	• Monitored natural attenuation. • Institutional controls to protect potential future receptors.	McNab et al., 1997a
Port Hueneme Naval Construction Battalion Center, NEX Gas Station	Coastal fluvial deltaic sediments. Semi-perched unconfined aquifer. Groundwater depth is about 15 ft bgs; relatively poor quality–1,200 mg/L TDS; flow velocity is high–about 0.5 to 1.0 ft/day.	Former underground fuel piping at base service station. Approx. 11,000 gal of gasoline released from 1984–1985. Over excavation performed during tank removal and upgrade. Free product present covering an areal extent of roughly 500 × 500 ft.	Dissolved BTEX plume about 1,000 ft long; MTBE plume over 4,000 ft long, possibly extending along buried gravel stream channel.	MTBE Plume has potential to impact harbor drainage canal ecosystem.	Location of abandoned agricultural wells that may provide pathway to regional aquifer. What are appropriate risk management activities for National Test Site? What are impacts of MTBE to drainage canal marine ecosystem?	Dissolved plume BTEX concentrations are decreasing. The site is part of the National Test Site Program and the plume will be used to test various remediation technologies.	• No further action on BTEX plume. • Monitor MTBE Plume for two years for stability.	Everett et al., 1998

Table D-1. (Continued)

Site name	Hydrogeologic setting	Exposure: Primary source and residual hydrocarbons	Exposure: Potential pathways	Exposure: Potential receptors	Key issues	Risk assessment findings	Recommendations	References
Presidio at San Francisco Building 637 Area	**Tidal wetland/esturine depositional sediments and fill. Approx. 750 ft from San Francisco Bay. Approx. 550 ft from proposed constructed wet lands. Depth to water about 5 ft.**	**Ruptured piping during 1989 Loma Prieta earthquake. Unknown quantity of diesel and gasoline released. Extensive over excavation during tank and piping removal. Currently, free product present. TPH analysis confused by high organic content of soils.**	**Low concentrations of BTEX components in groundwater. TPH-gasoline measured to the 100 μg/L concentration contour is about 600 ft long.**	**No existing receptors have been identified. Potential to impact planned constructed wetlands.**	**Will there be hydraulic changes during wetlands construction? Where is the benzene?**	**Plume stability data not available. Strong secondary evidence of passive biodegradation of petroleum hydrocarbons. High retardation due to organic rich soils. Aquitards prevent impact to regional aquifers. Any vertical migration appears to be upward. Impact on proposed constructed wetlands not likely.**	**• Additional monitoring to verify plume stability. • Monitored natural attenuation. • Institutional controls to protect potential future receptors.**	**Small et al., 1998**
Travis Air Force Base North/South Gas Stations	**Alluvial unconsolidated clays, silts, sands, and gravels. Clay and shale aquitards underlies the site. Depth to water about 15 ft.**	**Former underground fuel tanks and piping at two base service stations. Unknown quantity of gasoline released. The volume of the release is unknown. Extensive over excavation during tank removal and upgrade. Two inches of free product observed in monitoring wells near former UST at south gas station.**	**Only 24 months of monitoring - Plume stability data not available. Co-mingled plumes from North and South Gas Stations–600 ft long from up-gradient site, 380 ft from down-gradient site. MTBE detected in vicinity of UST locations. MTBE plume smaller than BTEX plume. Inhalation pathway analyzed.**	**No existing receptors have been identified.**	**How long plume extend before it stabilizes? What techniques can be applied to evaluate passive bioremediation potential? Are there vertical gradients and if so, which way do they flow? Time to cleanup key technical issue.**	**Strong secondary evidence of passive biodegradation of petroleum hydrocarbons. Estimate about 30 yr. for BTEX concentrations to reach MCLs. Aquitards prevent impact to regional aquifers; any vertical migration appears to be upward. Inhalation exposure is not a concern.**	**• Installation of two down gradient sentry wells. • Additional monitoring to verify plume stability. • Monitored natural attenuation. • Institutional controls to protect potential future receptors.**	**McNab et al., 1997b**

Table D-1. (Continued)

Site name	Hydrogeologic setting	Exposure: Primary source and residual hydrocarbons	Exposure: Potential pathways	Exposure: Potential receptors	Key issues	Risk assessment findings	Recommendations	References
Vandenberg Air Force Base Exchange Gas Station	**Uplifted marine terrace consisting of layers of sand and clay. Shallow perched saturated zone, 15 ft thick, sits on fat clay layer. Sampling to 60 ft below this layer indicate unsaturated conditions. Depth to top of perched groundwater is seasonally variable. Depth to regional groundwater is 450 ft. Perched groundwater of relatively poor quality—About 1,100 mg/L TDS.**	**Former underground fuel tanks and piping at base service station. Estimated 2,300 gal of gasoline released over unknown period of time. Over excavation performed during tank removal. Hydrocarbon sheen noted in some vadose zone samples.**	**Dissolved BTEX and MTBE groundwater plumes are less than about 300 ft long.**	**No existing receptors have been identified. Nearest groundwater basin being used is 3 miles away.**	**What are beneficial uses of perched, low yield aquifer created by lawn irrigation and car wash? What is the time frame for anticipated use, if ever, for perched aquifer?**	**Strong secondary evidence of passive biodegradation of petroleum hydrocarbon compounds. Evidence of plume capture by transpiration of nearby eucalyptus trees. Aquitards prevent impact to regional aquifers. Existing 14 extraction well field yields combined yield of about 2 gal/min; pump and treat remedial alternative is impractical. MTBE Plume overlaps BTEX plume; MTBE plume expected to detach from BTEX plume. MTBE plume expected to stabilize through dispersion.**	**• Monitored natural attenuation with possible phytoremediation. • Removing sources of perched aquifer recharge allowing aquifer to dewater.**	**McNab et al., 1998b**

D-2. References

Everett, L. G., S. J. Cullen, D. W. Rice, W. W. McNab, B. P. Dooher, M. C. Kavanaugh, P. C. Johnson, W. E. Kastenberg, and M. C. Small (1998), *Risk-Based Assessment of Appropriate Fuel Hydrocarbon Cleanup Strategies for the Naval Exchange Gasoline Station, Naval Construction Battalion Center, Port Hueneme, California*, Lawrence Livermore National Laboratory, Livermore, Calif. (UCRL-AR-130891).

Johnson, P. C., D. W. Rice, W. W. McNab, L. G. Everett, M. C. Kavanaugh, W. E. Kastenberg, M. C. Small, and S. J. Cullen (1998), *Risk-Based Assessment of Appropriate Fuel Hydrocarbon Cleanup Strategies for the Petroleum, Oils, and Lubricants Yard, Castle Airport*, *California*, Lawrence Livermore National Laboratory, Livermore, Calif. (UCRL-JC-131034).

Kavanaugh, M. C., D. W. Rice, W. W. McNab, M. C. Small, S. J. Cullen, P. C. Johnson, L. G. Everett, and W. E. Kastenberg (1998a), *Risk-Based Assessment of Appropriate Fuel Hydrocarbon Cleanup Strategies for Site 390, Marine Corps Air Station (MCAS) El Toro, California*, Lawrence Livermore National Laboratory, Livermore, Calif. (UCRL-AR-129151).

Kavanaugh, M. C., W. W. McNab, D. W. Rice, P. C. Johnson, M. C. Small, W. E. Kastenberg, L. G. Everett, and S. J. Cullen (1998b), *Risk-Based Assessment of Appropriate Fuel Hydrocarbon Cleanup Strategies for China Lake Naval Air Weapons Station, Navy Exchange Gas Station Site*, Lawrence Livermore National Laboratory, Livermore, Calif. (UCRL-AR-129578).

McNab, W. W., B. P. Dooher, D. W. Rice, M. C. Kavanaugh, P. C. Johnson, S. J. Cullen, L. G. Everett, and W. E. Kastenberg (1997a), *Assessment of Appropriate Fuel Hydrocarbon Cleanup Strategies for George Air Force Base, Victorville, California, Using a Risk-Based Approach*, Lawrence Livermore National Laboratory, Livermore, Calif. (UCRL-AR-125619).

McNab, W. W., B. P. Dooher, D. W. Rice, M. C. Kavanaugh, S. J. Cullen, L. G. Everett, W. E. Kastenberg, M. C. Small, and P. C. Johnson (1997b), *Assessment of Appropriate Fuel Hydrocarbon Cleanup Strategies for Travis Air Force Base, Fairfield, California, Using a Risk-Based Approach*, Lawrence Livermore National Laboratory, Livermore, Calif. (UCRL-AR-125941).

McNab, W. W., B. P. Dooher, D. W. Rice, S. J. Cullen, L. G. Everett, M. C. Kavanaugh, W. E. Kastenberg, M. C. Small, and P. C. Johnson (1998b), *Risk-Based Assessment of Appropriate Fuel Hydrocarbon Cleanup Strategies for Base Exchange Gas Station Site, Vandenberg Air Force Base*, California, Lawrence Livermore National Laboratory, Livermore, Calif. (UCRL-AR-126774).

McNab, W. W., D. W. Rice, S. J. Cullen, L. G. Everett, P. C. Johnson, W. E. Kastenberg, M. C. Kavanaugh, M. C. Small, and Tina M. Carlsen (1998a), *Risk-Based Assessment of Appropriate Fuel Hydrocarbon Cleanup Strategies for Area 43 MWR Gas Station, Marine Corps Base, Camp Pendleton*, California. Lawrence Livermore National Laboratory, Livermore, Calif. (UCRL-AR-128220).

Pelmulder, S., W. W. McNab, Small, M. C., W. E. Kastenberg, D. W. Rice, M. C. Kavanaugh, P. C. Johnson, L. G. Everett, and S. J. Cullen (1998), *Risk-Based Assessment of Appropriate Fuel Hydrocarbon Cleanup Strategies for Tank 325 Site at Nebo Annex, Marine Corps Logistic Base*, Barstow, California. Lawrence Livermore National Laboratory, Livermore, Calif. (UCRL-AR-129579).

Small, M. C., W. W. McNab, D. W. Rice, S. J. Cullen, L. G. Everett, M. C. Kavanaugh, W. E. Kastenberg, and P. C. Johnson (1998), *Risk-Based Assessment of Appropriate Fuel Hydrocarbon Cleanup Strategies for Presidio at San Francisco, Building 637 Area*, Lawrence Livermore National Laboratory, Livermore, Calif. (UCRL-AR-129152).

Appendix E

Assessment of Fuel Hydrocarbon Plume Behavior and Biodegradation Rates

Appendix E
Section E-1

Comparisons of Geochemical Signatures of Biotransformation of Hydrocarbon in Groundwater

Appendix E (Section E-1)

Comparisons of Geochemical Signatures of Biotransformation of Hydrocarbon in Groundwater

E-1.1. Introduction

Fuel hydrocarbon compounds from leaking tanks and pipelines are common groundwater contaminants. Recently, much interest has developed in utilizing natural attenuation processes to remediate groundwater contaminated with fuel hydrocarbons as opposed to active engineered solutions such as pump-and-treat technology. Natural attenuation includes biotransformation processes which are known from numerous field and laboratory studies to affect fuel hydrocarbons (e.g., Reinhard, Goodman, and Barker, 1984; Barker and others, 1986; Major et al., 1988; Grbic-Galic and Vogel, 1991; Haag et al., 1991; Kazumi et al., 1997). Statistical analyses of large populations of FHC plumes released from leaking underground fuel tanks have shown that fuel hydrocarbon plume lengths are generally limited in extent, presumably as a result of biotransformation processes (Rice et al., 1995; Buscheck et al., 1996; Mace et al., 1997).

Identifying evidence of fuel hydrocarbon biotransformation from field data is a key element in formulating risk management strategies that incorporate natural attenuation at groundwater contamination sites. Primary evidence of biotransformation (i.e., observed decline in total contaminant mass over time) is often difficult to extract from monitoring data because of sparse sampling networks and short sampling histories. Therefore, secondary lines of evidence must often be pursued. Secondary evidence consists of changes in groundwater geochemistry associated with the FHC plume which may reflect the oxidation of fuel hydrocarbons by microorganisms (e.g., Vroblesky and Chapelle, 1994; Borden et al., 1995). For example, the mineralization of toluene, a soluble and biodegradable gasoline constituent, to carbon dioxide could include a number of potential mechanisms:

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

$$C_7H_8 + 18MnO_2 + 36H^+ \rightarrow 7CO_2 + 18Mn^{2+} + 22H_2O \qquad \text{(E-1-2)}$$

$$5C_7H_8 + 36NO_3^- + 36H^+ \rightarrow 35CO_2 + 18N_2(g) + 38H_2O \qquad \text{(E-1-3)}$$

$$C_7H_8 + 36Fe(OH)_3 + 72H^+ \rightarrow 7CO_2 + 36Fe^{2+} + 94H_2O \qquad \text{(E-1-4)}$$

$$2C_7H_8 + 9SO_4^{2-} + 18H^+ \rightarrow 14CO_2 + 9H_2S + 8H_2O \qquad \text{(E-1-5)}$$

$$2C_7H_8 + 10H_2O \rightarrow 14CO_2 + 9CH_4 \qquad \text{(E-1-6)}$$

Laboratory studies have confirmed that fuel hydrocarbons may biotransform through reactions involving a variety of specific electron acceptors (e.g., Lovley et al., 1989; Beller et al., 1992, Lovley et al., 1995; Vroblesky et al., 1996). Groundwater chemical constituents which serve as biotransformation 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 fuel hydrocarbon biotransformation, is often not measurable because of the low solubility of sulfide-bearing minerals under the E_h-pH conditions encountered in typical groundwater environments.

Each of these indicator parameters is subject to a certain degree of variability in background concentrations. Given the sparse monitoring well network often associated with fuel hydrocarbon releases, it may often be difficult to discern patterns in spatial distributions of geochemical indicators which offer unequivocal proof of biotransformation. To address this issue, variability in geochemical indicator species has been evaluated from six sites at military bases in California where releases of fuel hydrocarbons to groundwater from leaking underground fuel tanks (LUFTs) have been observed (Table E-1.1). The sites include the Area 43 Gas Station at Camp Pendleton Marine Corps Base (PMCB), the Petroleum, Oils, and Lubricants Fuel Farm Area at Castle Air Force Base (CAFB) near Merced, the Operable Unit 2 area at George Air Force Base (GAFB) near Victorville, the Building 637 area at the Presidio of San Francisco (PSF), the North-South Gas Stations at Travis Air Force Base (TAFB) near Fairfield, and the Base Exchange Service Station at Vandenberg Air Force Base (VAFB) near Lompoc. At each site, total petroleum hydrocarbons (TPH) were measured by gas chromatography. Geochemical indicator parameters were also measured, typically by ion chromatography or atomic adsorption spectroscopy (for ionic species and metals), although not all of the geochemical indicator parameters were available from all the sites. In general, groundwater quality data were available for only two to three years for most of the sites, whereas the likely period of release history spanned many decades as indicated by the site histories.

E-1.2. Analysis

E-1.2.1. Geochemical Evidence of Biotransformation

Consider the hypothetical fuel hydrocarbon plume depicted on Figure E-1.1. As the release occurs, the more soluble components (e.g., benzene, toluene) will dissolve into groundwater and begin to migrate downgradient via advective and dispersive transport. Contemporaneously, indigenous microbiota metabolize the dissolved hydrocarbon constituents for energy and cell mass. As a result, electron acceptors are sequentially depleted in general accordance with the reactions listed in Eqs. E-1-1 through E-1-6. Ideally, the spatial distribution of geochemical indicators would reflect the changes in electron acceptor concentrations, redox conditions, and mineralization associated with the biotransformation reactions. In reality, physical and biogeochemical heterogeneities, as well as complex boundary conditions, would produce a less coherent distribution of geochemical indicator values. The interpretation of these spatial distributions would also be affected by the limited sampling resolution offered by the monitoring well networks typically installed at LUFT sites. In addition, even if adequate time series data were available, identifying temporal trends indicative of biotransformation would also be problematic in many instances. Because of the release scenarios associated with LUFTs – percolation of light non-aqueous phase liquids (LNAPLs) through the vadose zone to the water table – residual sources of contamination may persist as isolated ganglia or pools of LNAPL even after the LUFTs have been removed. Such sources could continue supplying dissolved-phase hydrocarbons to the aquifer over a period of decades. When coupled with biotransformation processes in the dissolved phase, this scenario may result in a pseudo-steady-state plume, where a dynamic mass balance exists between the influx of dissolved hydrocarbons from residual source dissolution and mass loss via biotransformation. Under this scenario, hydrocarbon concentrations could remain relatively stable over a long period.

Given these issues, one approach for identifying quantitative evidence of biotransformation process from a single sampling event is to compare median values of geochemical indicator parameters from monitoring wells located within the hydrocarbon plume with those which may be delineated as representing background. The use of median values for such a comparison offers the advantage of minimizing the influence of outlier values from either sample set in affecting the interpretation of the data. Differences between median values for a number of geochemical indicators that are consistent with Eqs. E-1-1 through E-1-6 would provide support for a biotransformation hypothesis.

For analyses of geochemical indicator data from the six LUFT sites, monitor wells characterized by detectable quantities of fuel hydrocarbons during the sampling round of interest were designated as plume interior wells. Those wells not exhibiting detectable fuel hydrocarbons were assumed to represent background conditions. Analysis of median concentrations for the geochemical indicator data available from the six LUFT sites strongly supports the assertion that fuel hydrocarbon biotransformation processes are active at each site. Median concentrations of dissolved oxygen (DO) from interior and background wells are shown on Figure E-1.2 for five of the six sites (dissolved oxygen data were not available from the Vandenberg AFB LUFT site). Median dissolved oxygen concentrations from plume interiors are less than the median background concentration at four of the sites. The exception to this pattern, the LUFT site at the Presidio of San Francisco, is located in an anaerobic environment that is rich in natural organic carbon (background DO < 0.5 mg/L). It is likely that under such conditions, reported concentrations of DO would simply reflect atmospheric contamination of the groundwater samples. Median concentrations of nitrate and sulfate are shown on Figures E-1.3 and E-1.4, respectively. These data suggest that both nitrate and sulfate concentrations are depleted within plume interiors compared to background at all six sites, possibly reflecting denitrification and sulfate reduction processes (Eqs. E-1-3 and E-1-5). Median concentrations of ferrous iron and manganese are shown on Figures E-1.5 and E-1.6, respectively; manganese data were not available from the LUFT site at the Camp Pendleton Marine Corps Base. Unlike the geochemical indicators which are aqueous-phase electron acceptors (i.e., DO, NO_3^-, SO_4^{2-}), the concentrations of dissolved iron and manganese become elevated as biotransformation reactions progress. This is because iron and manganese exist as electron acceptors in the solid phase (e.g., as $Fe(OH)_3$ or MnO_2) under ambient (generally aerobic) conditions. Reduction of these metals from their respective oxidized forms

(Fe^{3+}, Mn^{4+}) to the reduced forms (Fe^{2+}, Mn^{2+}) via Eqs. E-1-2 and E-1-4 results in mobilization and hence increased concentrations.

Median concentrations of dissolved methane are shown on Figure E-1.7. Elevated methane concentrations within the plume interior suggesting methanogenesis are evident at the LUFT sites at Camp Pendleton Marine Corps Base and especially at the Presidio of San Francisco. The strong indication of methanogenesis at the Presidio LUFT site is consistent with the background biogeochemical setting of the site (anaerobic, high natural organic carbon content), particularly given the relatively low concentrations of other electron acceptors such as nitrate and sulfate. Indeed, studies have shown that methanogenesis can become an important mechanism for the transformation of organic compounds if other electron acceptors are depleted (Baedecker et al., 1993; Zhang et al., 1998). Median redox potential (E_h) values are shown on Figure E-1.8. Viewed in isolation, E_h-values may be difficult to interpret because redox reactions are often not in equilibrium and it is difficult to ascertain which specific redox couple is responsible for the observed voltage potential on the E_h-electrode. Nevertheless, E_h measurements are useful as a semi-quantitative guide to the nature of the redox conditions at a particular site. E_h values are clearly lower within the plume interior at each of the sites in comparison to background, with the lowest background values observed at the two sites characterized by methanogenic processes which would be expected only under the most reducing conditions. Thus, observed values of E_h are also consistent with biotransformation (i.e., oxidation) reactions.

Median bicarbonate alkalinity values are shown on Figure E-1.9. Bicarbonate alkalinity is clearly elevated in the plume interiors at each of the sites in comparison to background. A likely explanation for this phenomenon is the dissociation of carbonic acid produced from the mineralization of the fuel hydrocarbons. This hypothesis is supported by the median values of pH observed in interior and background wells (Fig. E-1.10). The production of carbonic acid via mineralization, and the transient presence of trace organic acid intermediate transformation products of the fuel hydrocarbons, would be expected to lower the pH of the groundwater solution, although this would be moderated somewhat by the buffering effects of mineral phases such as calcite. Small differences in median pH values between plume interior wells and background are consistent with such expected pH differences for four of the five sites reporting pH values.

E-1.2.2. Comparison of Geochemical Indicators

The comparison of plume interior and background geochemical parameter values provides semi-quantitative evidence supporting biotransformation processes across several sites. However, in most instances the issue of biotransformation at individual sites will constitute the immediate problem of interest. Again, geochemical indicator parameters may be used to provide semi-quantitative evidence of biotransformation processes. In this case, the problem is one of examining the relationship between geochemical indicator values and hydrocarbon concentrations in individual groundwater samples from a given site.

Rank correlation coefficients describing the relationship between each geochemical indicator parameter and the concentration of TPH for an individual sampling round at each of the six sites are shown on Table E-1.2. Rank correlation was used because of the apparent lognormal distribution of many of the geochemical indicator species concentrations. Four of the parameters, redox potential, ferrous iron, manganese, and dissolved methane exhibit relatively high rank correlations versus TPH, with $r \geq 0.5$ for at least five of the six sites. The remaining parameters (dissolved oxygen, nitrate, sulfate, pH, and bicarbonate alkalinity) exhibit poorer correlation with TPH overall, with $r \leq 0.5$ for three or more of the six sites. Dissolved oxygen in particular appears to be a poor biotransformation indicator as quantified by correlation with TPH.

For five of the six sites in the study, approximately one-half of the monitoring wells were characterized by TPH concentrations less than the applicable detection limit (i.e., delineated as background wells). As such, the task of identifying meaningful correlations between geochemical indicator parameters and fuel hydrocarbon concentrations becomes more difficult. A logical alternative, therefore, is to divide the sample population for a given indicator into two sets: those associated with detections of TPH and those presumably representing background conditions. The two populations may then be compared using a standard test to ascertain whether or not the means of the two sets differ significantly. The students *t*-test is frequently used for this analysis, although in this case a non-parametric equivalent, the Kruskal-Wallis test, was used instead because of the lognormal distributions of many of the geochemical parameters. The confidence levels pertaining to the significance of differences in the means between the plume interior and background sample sets for each indicator at each site are shown on Table E-1.3 (confidence levels less than 90% were considered to not be significant). In general, these results match those suggested by the correlation analysis: redox potential, ferrous iron, manganese, and dissolved methane concentrations generally differ significantly between the two data sets, whereas oxygen, nitrate, sulfate, pH, and bicarbonate alkalinity often do not. However, these analyses also suggest differences in how the data are distributed at individual sites. For example, most of the indicator parameters at the Travis AFB LUFT site are easily distinguished between the plume interior and background wells, whereas those at the Presidio of San Francisco LUFT site are not. This suggests that patterns of biotransformation are not equally well-delineated between the sites, possibly reflecting spatial heterogeneities in various biogeochemical transformation regimes or differences in how monitoring wells are located relative to the morphology of the plume.

E-1.2. Discussion

Evaluations of the relationships between TPH concentrations and geochemical indicators by both correlation analyses and population means analyses suggest that redox potential, ferrous iron, manganese, and methane are more robust indicators than the other parameters. A likely explanation lies in the difficulty in distinguishing changes in groundwater geochemistry resulting from biotransformation with background fluctuations arising from other causes. In naturally aerobic groundwater settings, ferrous iron, manganese, and methane would be expected to exhibit very low concentrations, whereas those of sulfate and bicarbonate alkalinity may be relatively high. Thus, the biotransformation of small quantities of fuel hydrocarbons may generate a response in ferrous iron that is easily quantified, whereas the utilization of small quantities of sulfate compared to background may go unrecognized.

To test this explanation, a signal-to-noise parameter, Δ, may be defined, in principle, for geochemical indicators (exclusive of E_h and pH) at each site based on median background and median plume interior concentrations:

$$\Delta = \left| \frac{Median\,C_{bkg} - Median\,C_{plume}}{Median\,C_{bkg}} \right| \tag{E-1-7}$$

The ranges of rank correlation coefficients corresponding to the median value of Δ for each parameter at each site are shown on Figure E-1.12. In general, the parameters with Δ-values less than 0 (i.e., parameters with non-zero background concentrations which are depleted in the plume interior by biotransformation processes) exhibit poorer correlation with TPH concentrations than those with positive Δ-values. This is especially true for DO, where background concentrations are relatively low as a result of limited solubility. Because of the difficulty in accurately quantifying DO below approximately 0.5 mg/L in routine groundwater analyses, a very sharp difference between plume interior and background wells may be difficult to observe with relatively few wells overall. On the other hand, background sulfate concentrations are high enough that fuel hydrocarbon biotransformation only depletes a portion of the available sulfate. As a result, variability in background concentrations may match or exceed the concentration loss associated with sulfate reduction. Nitrate represents an intermediate case between oxygen and sulfate. Among the indicators exhibiting positive Δ-values, bicarbonate alkalinity is unique in that significant background concentrations are usually present. As a result, variability in background concentrations tends to reduce the correlation between bicarbonate alkalinity and fuel hydrocarbon concentrations. Correlations with fuel hydrocarbon concentrations are generally the highest with those compounds exhibiting the lowest background concentrations – manganese, methane, and ferrous iron.

The practical utility in these findings is in providing guidance to site investigators as to which geochemical biotransformation indicators are likely to be the most reliable. Future sampling at these sites or longer-term analyses at other sites may assist in confirming the findings. Time series analyses may also provide insights into possible seasonal effects that could influence the interpretation of the data. For example, seasonal changes in rainfall infiltration could alter the ambient groundwater chemistry to the extent that the dominant redox process responsible for biotransformation changes from one electron acceptor to another (e.g., Vroblesky and Chapelle, 1994).

References

Baedecker, M. J., Cozzarelli, I. M., and Eganhouse, R. P.: 1993, 'Crude oil in a shallow sand and gravel aquifer III. Biogeochemical reactions and mass balance modeling in anoxic groundwater,' *Applied Geochemistry*, **8**, 569–586.

Barker, J. F., Tessman, J. S., Plotz, P. E. and Reinhard, M.: 1986, 'The organic geochemistry of a sanitary landfill leachate plume,' *Journal of Contaminant Hydrology*, **1**(1/2), 171–189.

Beller, H. R., Grbic-Galic, D., and Reinhard, M.: 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., Gomez, C. A., and Becker, M.T.: 1995, 'Geochemical indicators of intrinsic bioremediation,' *Ground Water*, **33**(2), 180–189.

Buscheck, T. E., Wickland, D. C., and Kuehne, D. L.: 1996, 'Multiple lines of evidence to demonstrate natural attenuation of petroleum hydrocarbons,' *in Proceedings from the Conference on Petroleum Hydrocarbons and Organic Chemicals in Groundwater*, National Ground Water Association/API, Houston, Texas, November 13–15.

Grbic-Galic, D., and Vogel, T. M.: 1987, 'Transformation of toluene and benzene by mixed methanogenic cultures,' *Applied and Environmental Microbiology*, **53**(2), 254–260.

Haag, F., Reinhard, M., and McCarty, P. L.: 1991, 'Degradation of toluene and p-xylene in anaerobic microcosms: Evidence for sulfate as a terminal electron acceptor,' *Environmental Toxicology and Chemistry*, **10**(11), 1379–1390.

Kazumi, J., Caldwell, M. E., Suflita, J. M., Lovley, D. R., and Young, L. Y.: 1997, 'Anaerobic degradation of benzene in diverse anoxic environments,' *Environmental Science and Technology*, **31**(3), 813–818.

Langley, R.: 1970, *Practical Statistics*, Dover Publications, Inc., New York, New York, 399 p.

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

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

Mace, R. E., Fisher, R. S., Welch, D. M., and Parra, S. P.: 1997, 'Extent, Mass, and Duration of Hydrocarbon Petroleum Storage Tank Sites in Texas,' *Bureau of Economic Geology*, University of Texas at Austin.

Major, D.W., Mayfield, C. I., and Barker, J. F.: 1988, 'Biotransformation of benzene by denitrification in aquifer sand,' *Ground Water*, **26**(1), 8–14.

Miller, I., and Freund, J. E.: 1977, *Probability and Statistics for Engineers*, Second Edition, Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 529 p.

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

Reinhard, M., Goodman, N. L., and Barker, J. F.: 1984, ‘Occurrence and distribution of organic chemicals in two landfill leachate plumes,’ *Environmental Science and Technology*, **18**(12), 953–961.

Vroblesky, D. A., and Chapelle, F. H.: 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., Bradley, P. M., and Chapelle, F. H.: 1996, ‘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.

Zhang, C., Grossman, E. L., and Ammerman, J. W.: 1998, ‘Factors influencing methane distribution in Texas ground water,’ *Ground Water*, **36**(1), 58–66.

Table E-1.1. LUFT site overview.

LUFT site location	Nature of release (commencement of site operations)	Hydrogeologic setting	Sampling event for data used in this study	Number of plume interior wells, background wells	Analytes
Castle Air Force Base (CAFB)	**Aviation fuel (JP-4) leaking from above-ground and underground storage tanks, pipelines, and transfer lines (1940s)**	**Broad alluvial plain; mean depth-to-groundwater ~ 20 m**	**April, 1997**	**10, 9**	**TPH, BTEX, HCO_3^- (as alkalinity), CH_4, E_h, Fe^{2+}, Mn^{2+}, O_2, NO_3^-, pH, SO_4^{2}**
George Air Force Base (GAFB)	**Aviation fuel (JP-4) leaking from fueling pits and associated piping (mid-1950s)**	**High desert alluvial fan; mean depth to groundwater ~ 40 m**	**March, 1992 – August, 1995 (mean values)**	**(8)[1], (8)**	**TPH, BTEX, HCO_3^- (as alkalinity), CH_4, E_h, Fe^{2+}, Mn^{2+}, O_2, NO_3^-, pH, SO_4^{2}**
Camp Pendleton Marine Corps Base (PMCB)	**Base gasoline service station; leaks from underground tanks and piping systems (late 1950s)**	**Coastal canyon alluvium and fill; mean depth-to-groundwater ~ 5 m**	**April, 1997**	**8, 7**	**TPH, BTEX, HCO_3^- (as alkalinity), CH_4, E_h, Fe^{2+}, O_2, NO_3^-, SO_4^{2}**
Presidio of San Francisco (PSF)	**Gasoline and diesel released from above-ground storage tanks and piping systems (late 1930s)**	**Shallow marine deposits, organic-rich; mean depth-to-water ~ 1.5 m**	**April, 1997**	**7, 6**	**TPH, BTEX, HCO_3^- (as alkalinity), CH_4, E_h, Fe^{2+}, Mn^{2+}, O_2, NO_3^-, pH, SO_4^{2}**
Travis Air Force Base (TAFB)	**Base gasoline service station; leaks from underground tanks and piping systems (late 1960s)**	**Broad alluvial plain; mean depth-to-groundwater ~ 4 m**	**August-September, 1995**	**13, 16**	**TPH, BTEX, HCO_3^- (as alkalinity), CH_4, E_h, Fe^{2+}, Mn^{2+}, O_2, NO_3^-, pH, SO_4^{2}**
Vandenberg Air Force Base (VAFB)	**Base gasoline service station; leaks from underground tanks and piping systems (late 1960s)**	**Shallow marine deposits; mean depth-to-groundwater ~ 3 m**	**September, 1996**	**5, 9**	**TPH, BTEX, HCO_3^- (as alkalinity), CH_4, E_h, Fe^{2+}, Mn^{2+}, NO_3^-, pH, SO_4^{2}**

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[1] Data from background wells with TPH concentrations below the applicable detection limit were not available from the George AFB LUFT site. Therefore, for comparative purposes, the median TPH concentration (approximately 0.1 ppm) was selected to delineate the plume interior well set from background.

Table E-1.2. Rank correlation coefficients between geochemical parameter values and TPH at the six LUFT sites.

Parameter	Expected correlation	CAFB	GAFB	PMCB	PSF	TAFB	VAFB
DO	–	-0.394	-0.382	-0.490	0.078	-0.326	N.A.[1]
NO_3^-	–	-0.648	-0.811	-0.181	-0.132	-0.562	-0.452
SO_4^{2-}	–	-0.760	-0.709	-0.403	0.202	-0.274	-0.694
pH	–	-0.176	-0.598	N.A.	-0.444	0.030	-0.387
E_h	–	-0.563	-0.891	-0.916	-0.334	-0.746	-0.830
Fe^{2+}	+	0.556	0.493	0.831	0.638	0.817	0.825
Mn^{2+}	+	0.559	0.737	N.A.	0.595	0.601	0.771
CH_4	+	0.668	0.591	0.811	0.272	0.791	0.597
Alkalinity	+	0.571	0.497	0.718	0.445	0.549	0.190

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[1] N.A. = not analyzed or not available.

Table E-1.3. Kruskal-Wallis confidence levels that geochemical parameter values differ significantly between plume interior and background samples.

Parameter	CAFB	GAFB	PMCB	PSF	TAFB	VAFB
DO	not signf.	not signf.	not signf.	not signf.	>90%	N.A.[1]
NO_3^-	95%	99%	not signf.	not signf.	99%	not signf.
SO_4^{2-}	99%	95%	not signf.	not signf.	not signf.	95%
pH	not signf.	95%	N.A.	90%	not signf.	not signf.
E_h	99%	99%	99%	not signf.	99%	99%
Fe^{2+}	95%	not signf.	90%	90%	99%	99%
Mn^{2+}	90%	90%	N.A.	90%	99%	99%
CH_4	99%	not signf.	95%	90%	99%	90%
Alkalinity	95%	not signf.	95%	not signf.	99%	not signf.

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[1] N.A. = not analyzed or not available.

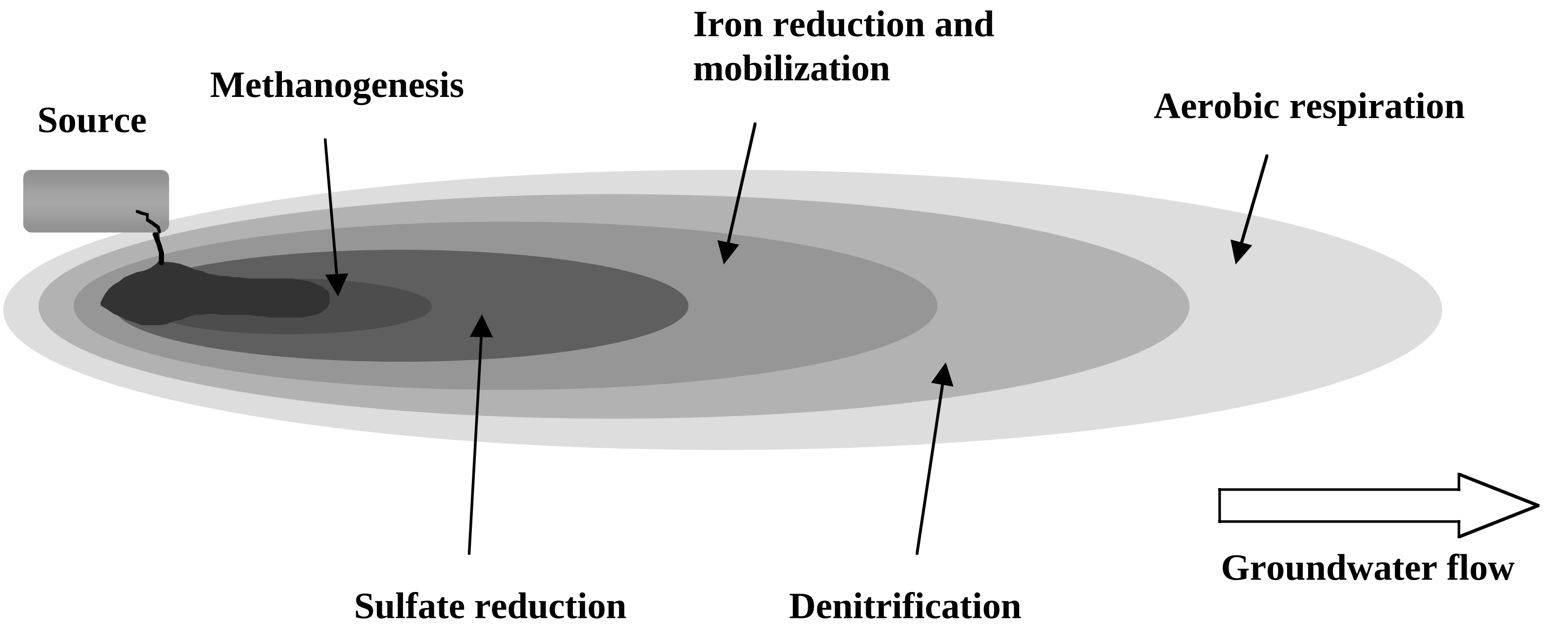

Figure E-1.1. A hypothetical fuel hydrocarbon release to groundwater with the associated impact on the local hydrogeochemistry.

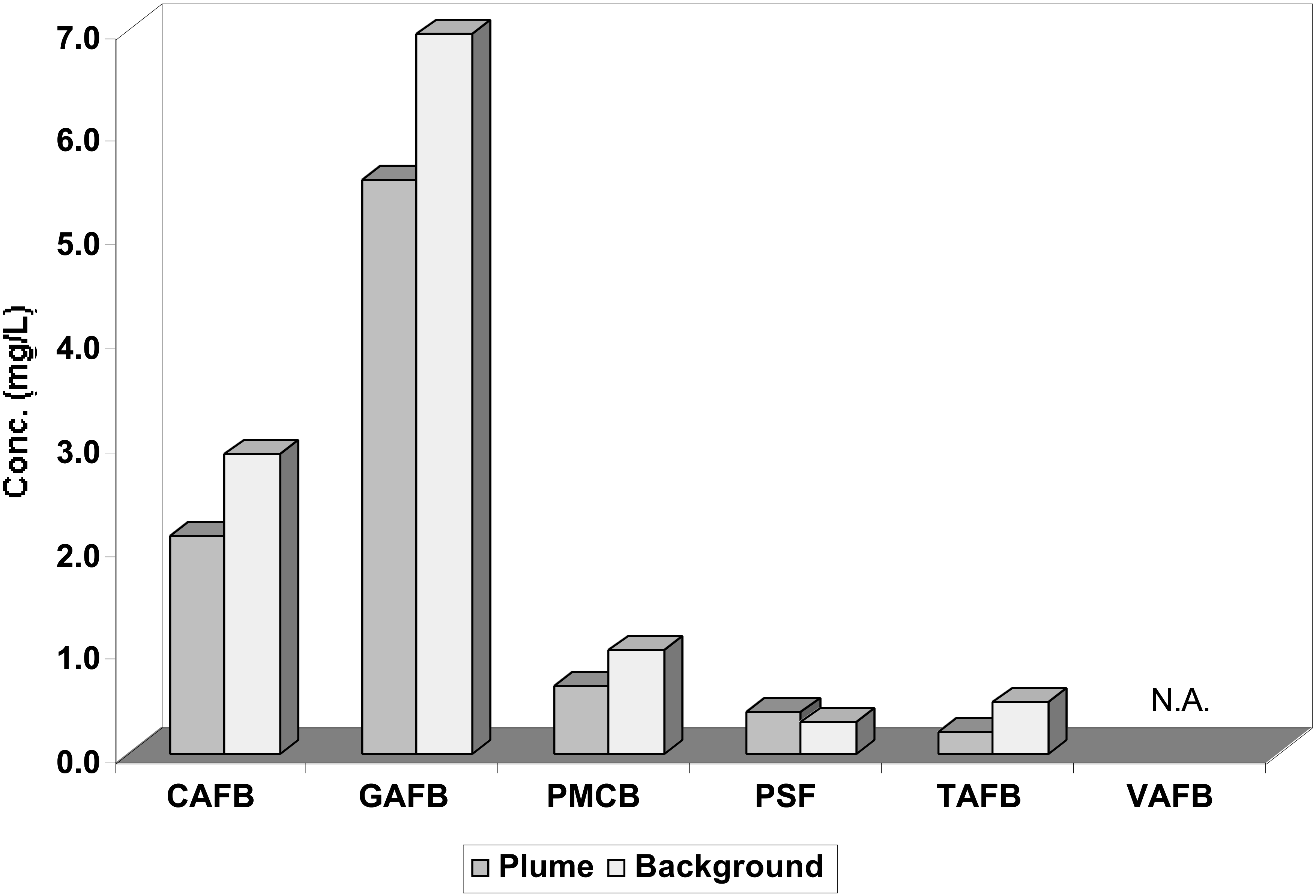

Figure E-1.2. Dissolved oxygen: comparison between median values from plume interior wells and median values from background wells.

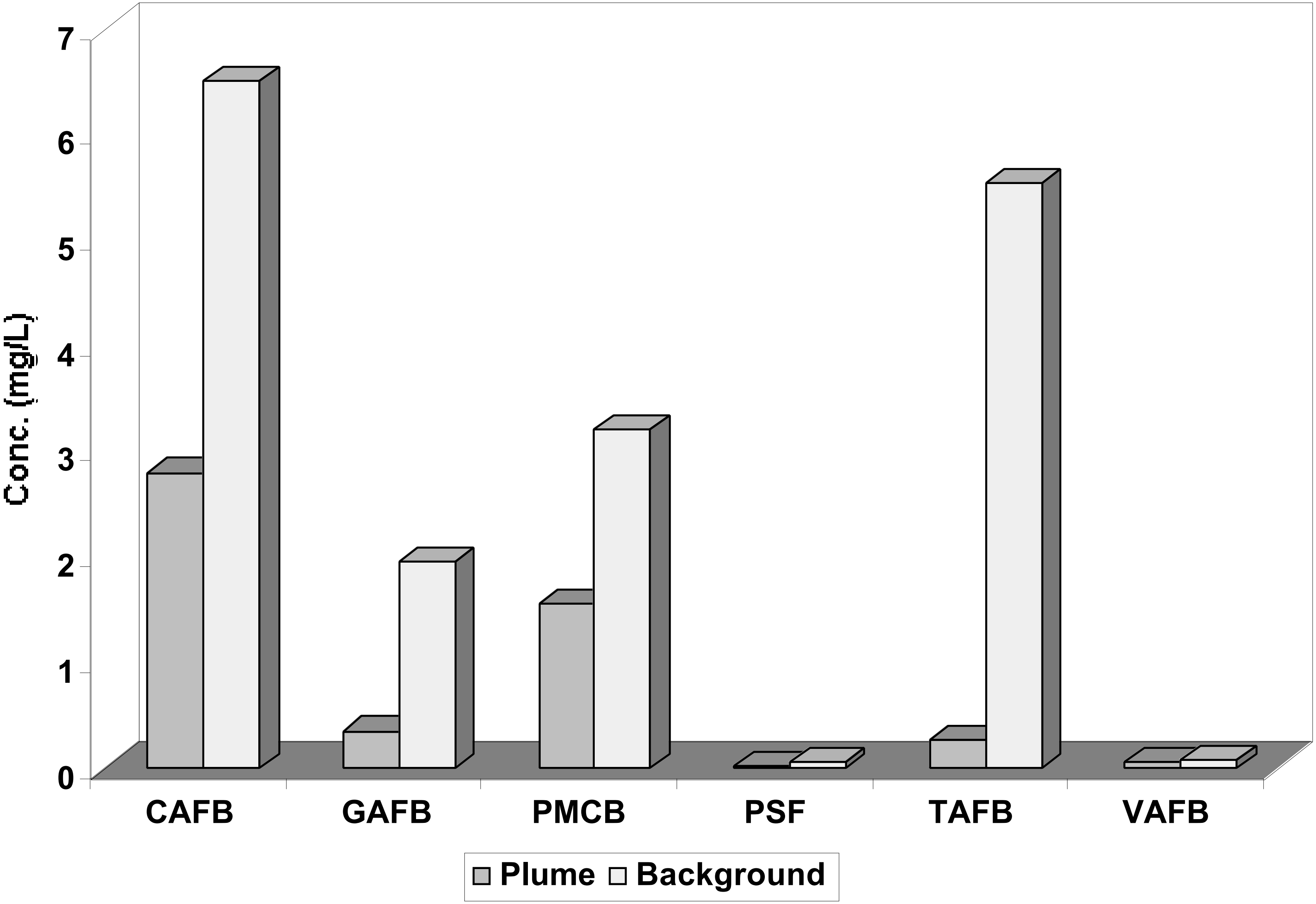

Figure E-1.3. Nitrate: comparison between median values form plume interior wells and median values form background wells.

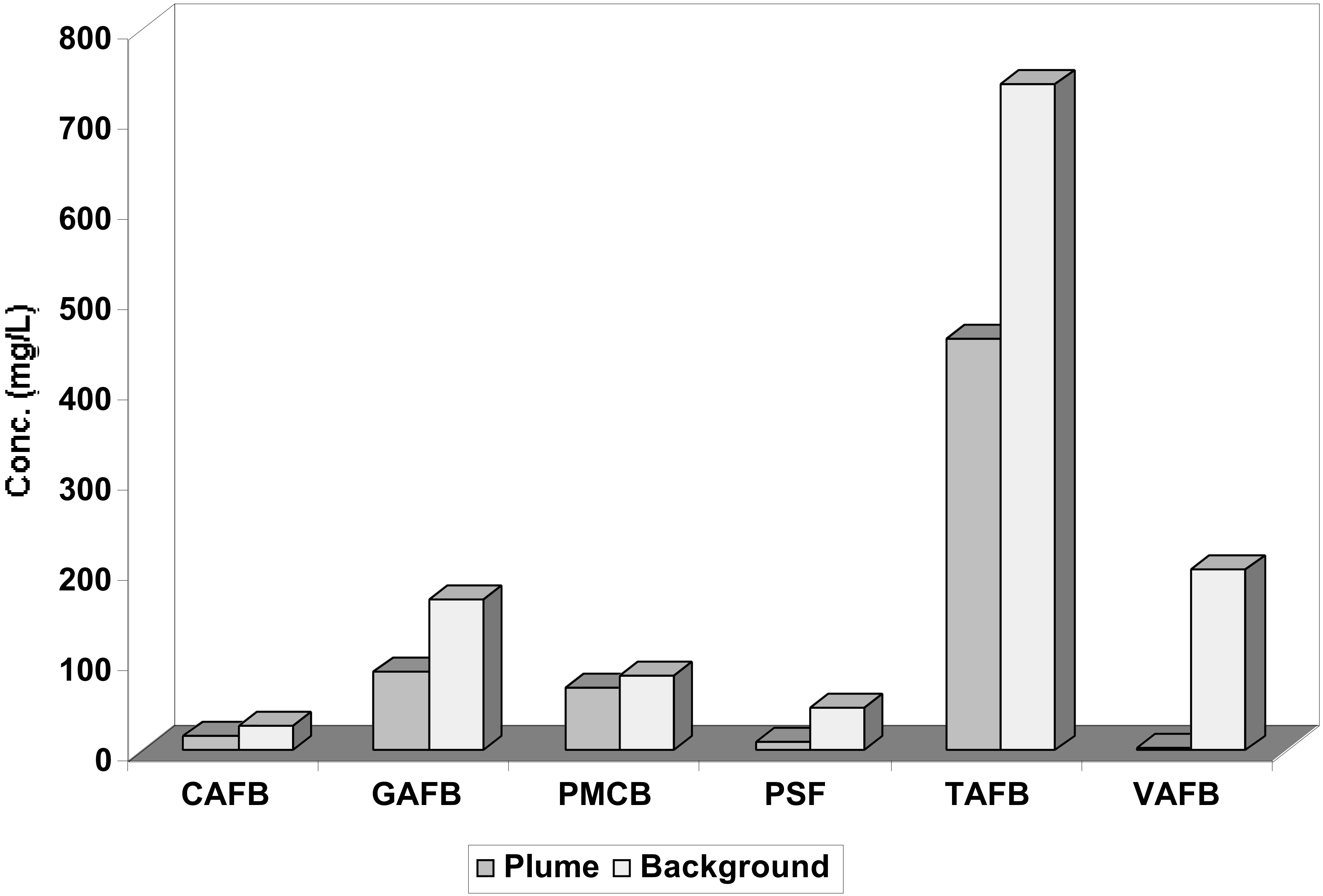

Figure E-1.4. Sulfate: comparison between median values from plume interior wells and median values from background wells.

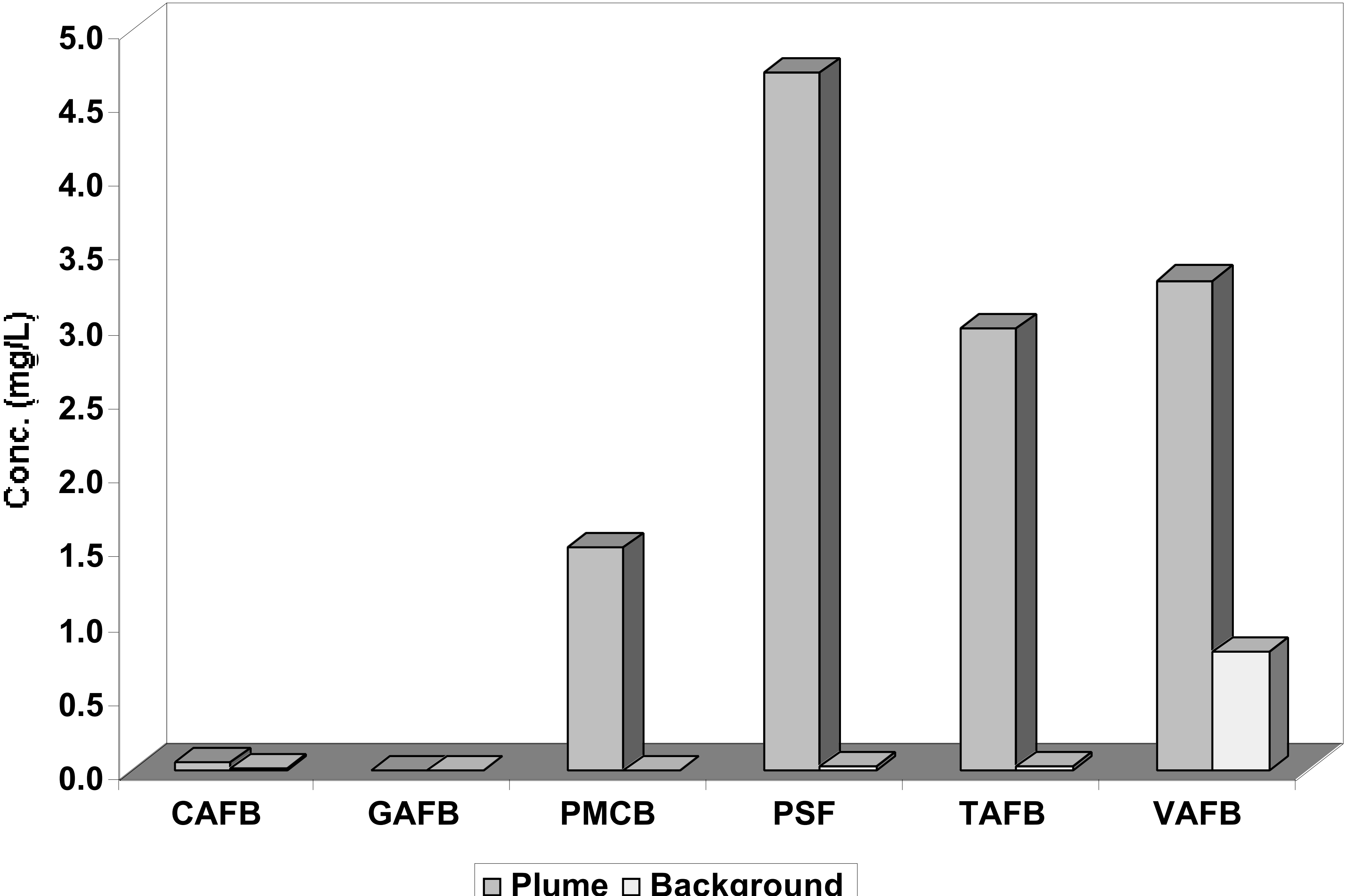

Figure E-1.5. Ferrous iron: comparison between median values from plume interior wells and median values from background wells.

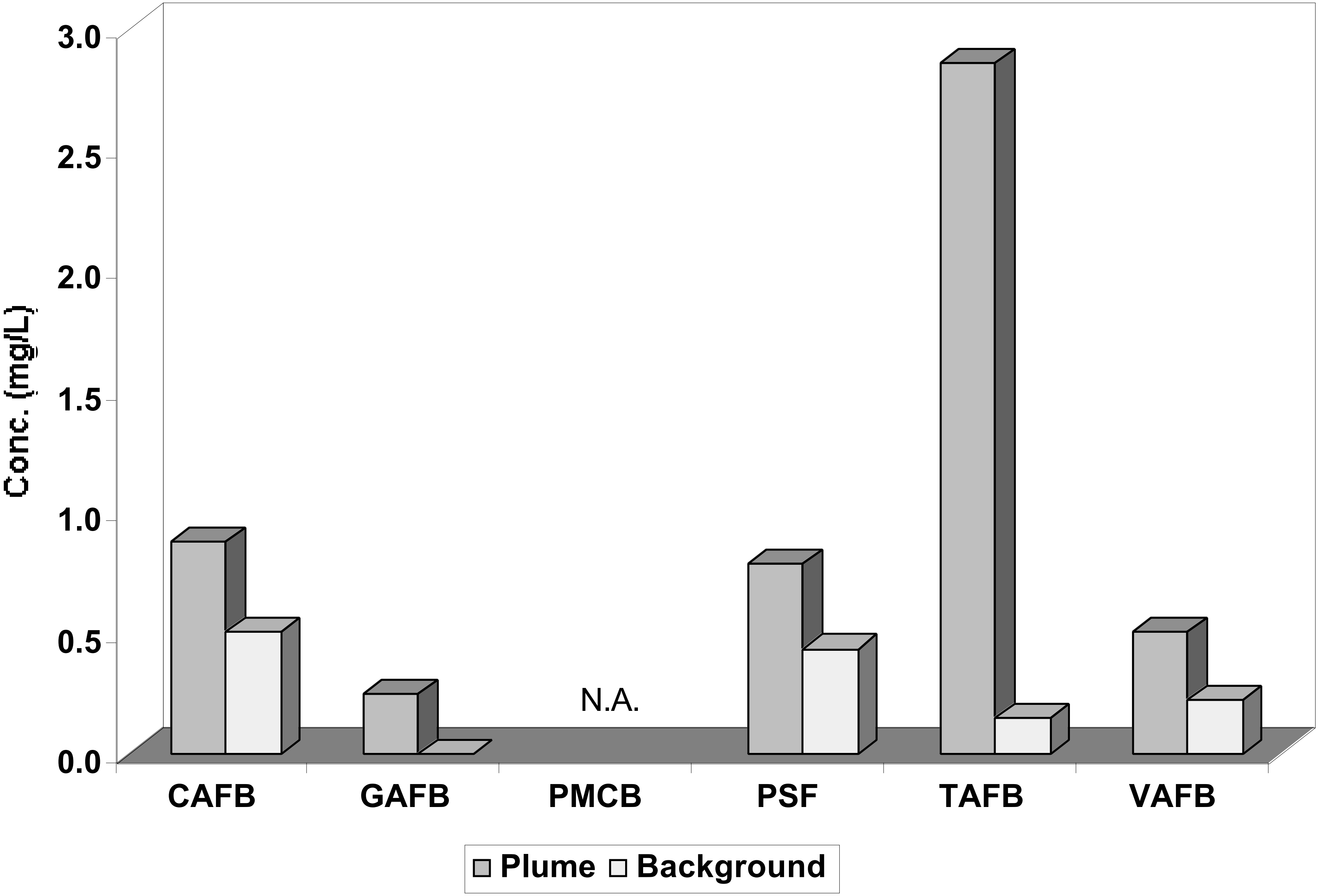

Figure E-1.6. Manganese: comparison between median values from plume interior wells and median values from background wells.

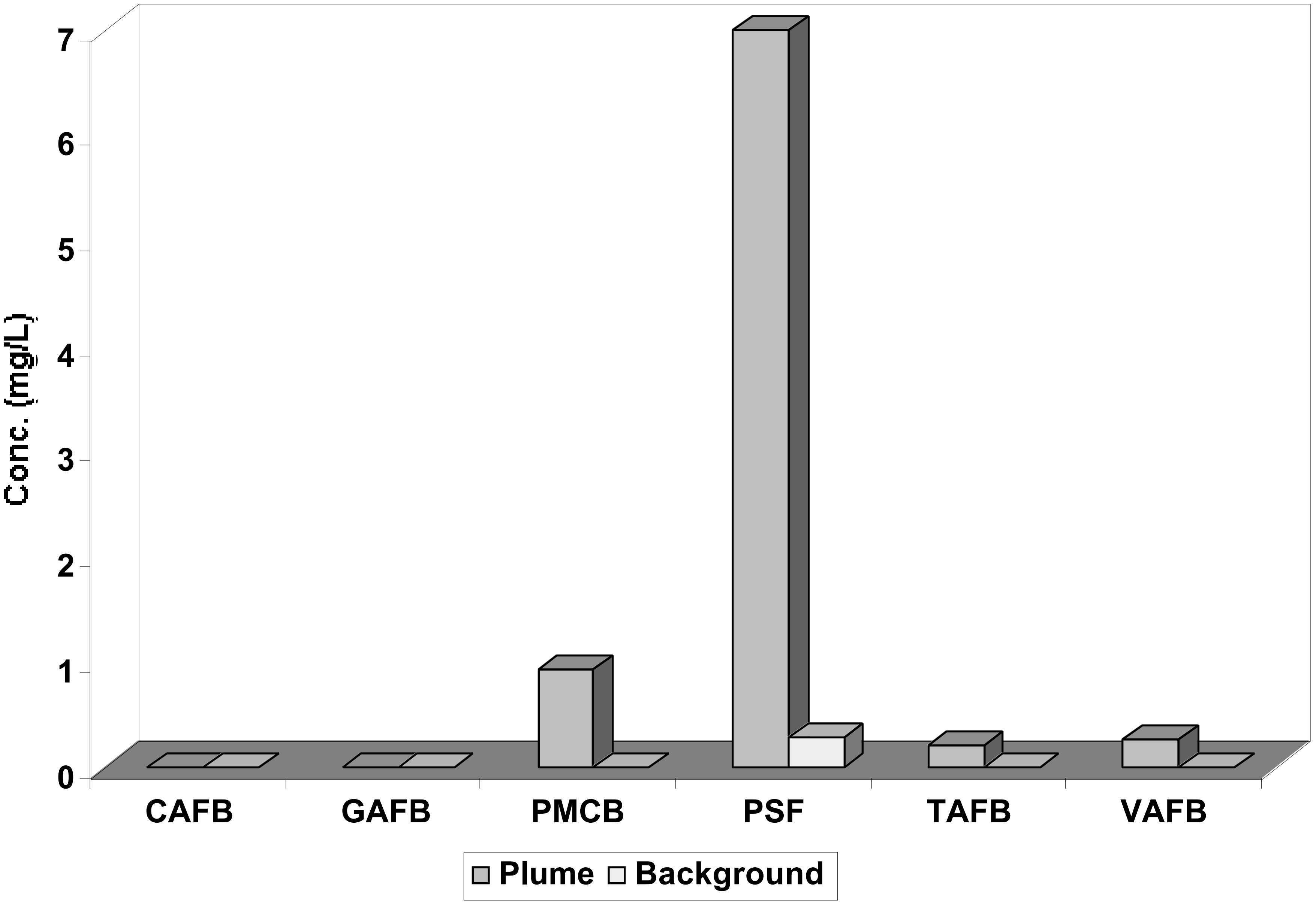

Figure E-1.7. Dissolved methane: comparison between median values from plume interior wells and median values from background wells.

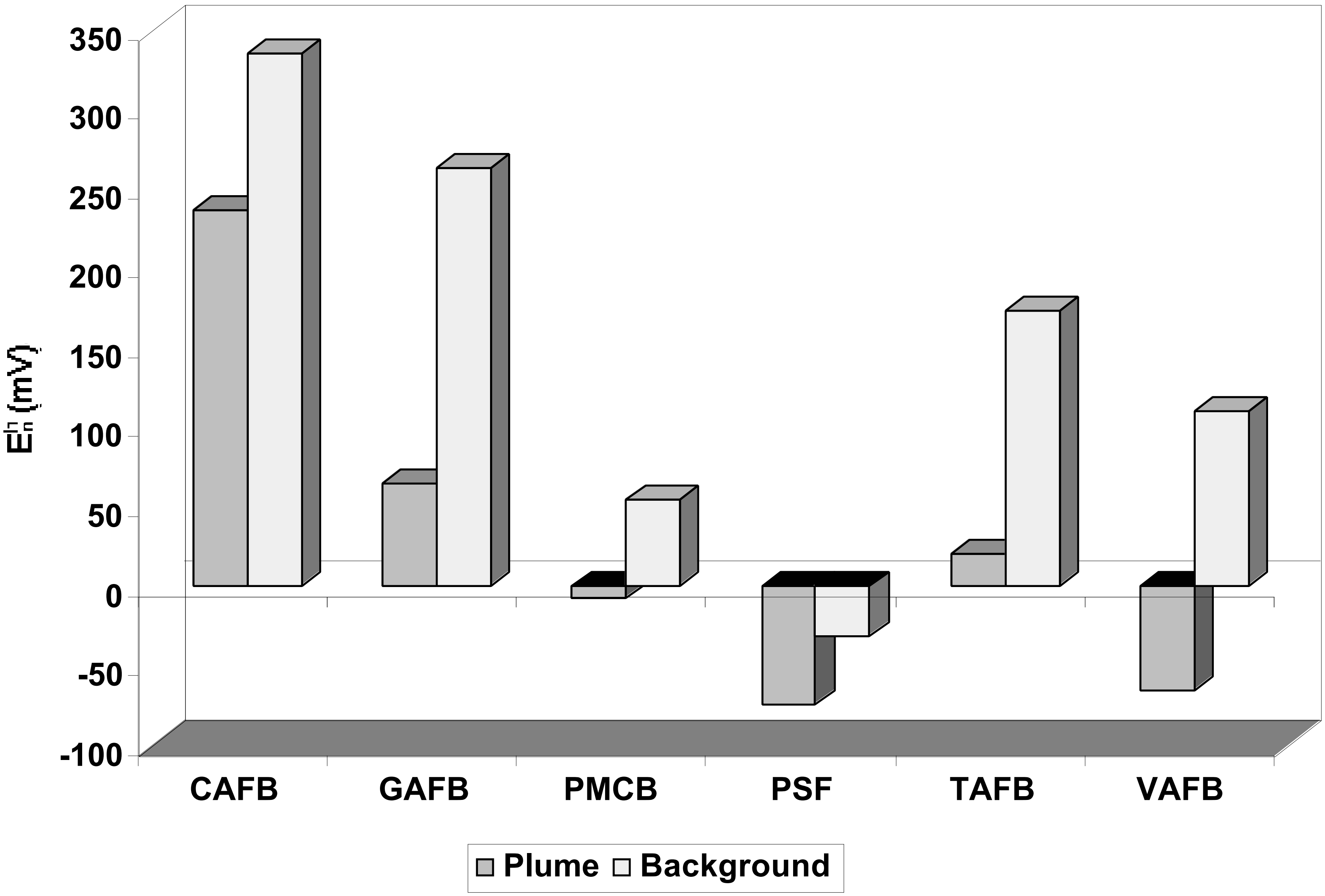

Figure E-1.8. E_h: comparison between median values from plume interior wells and median values from background wells.

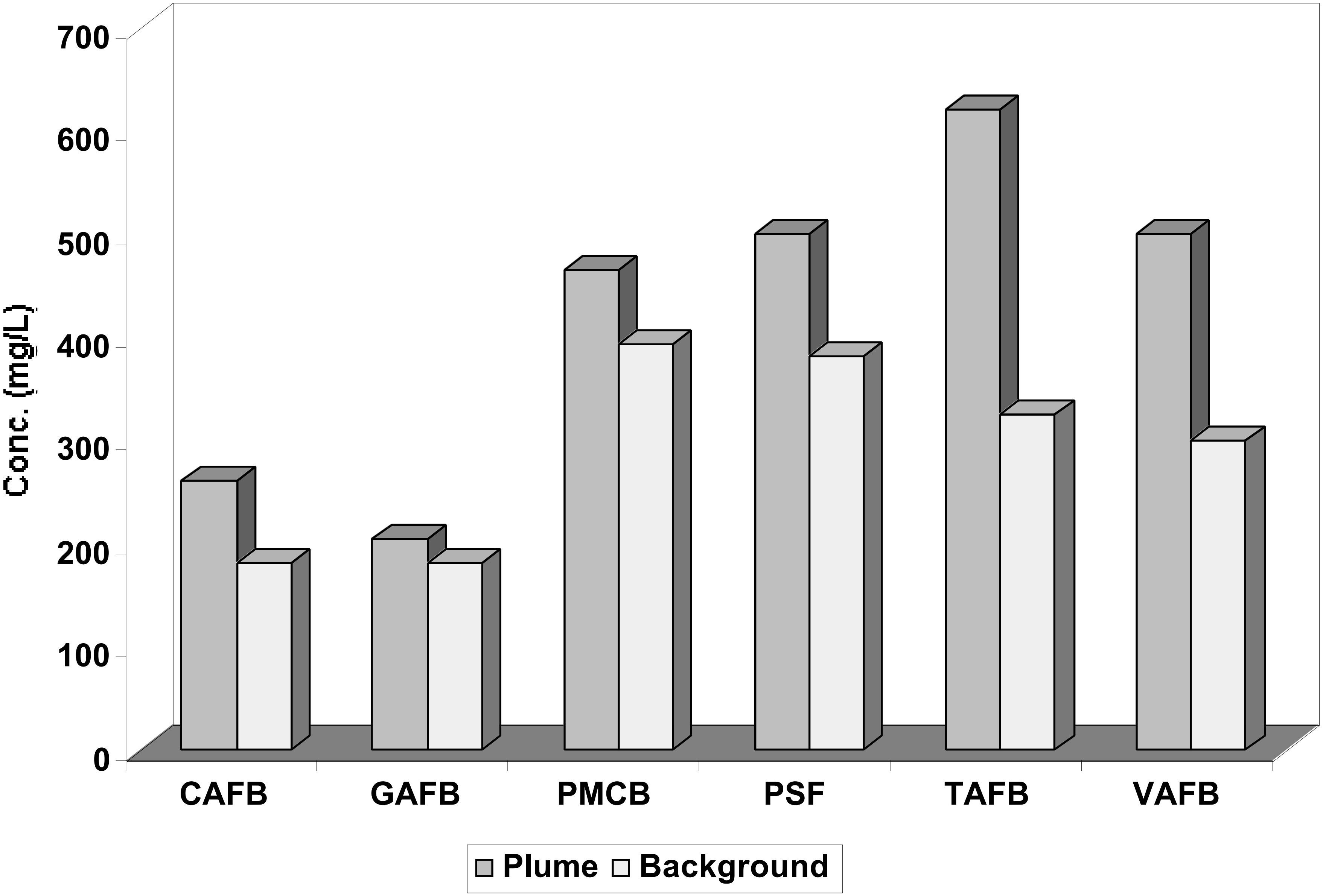

Figure E-1.9. Bicarbonate alkalinity: comparison between median values from plume interior wells and median values from background wells.

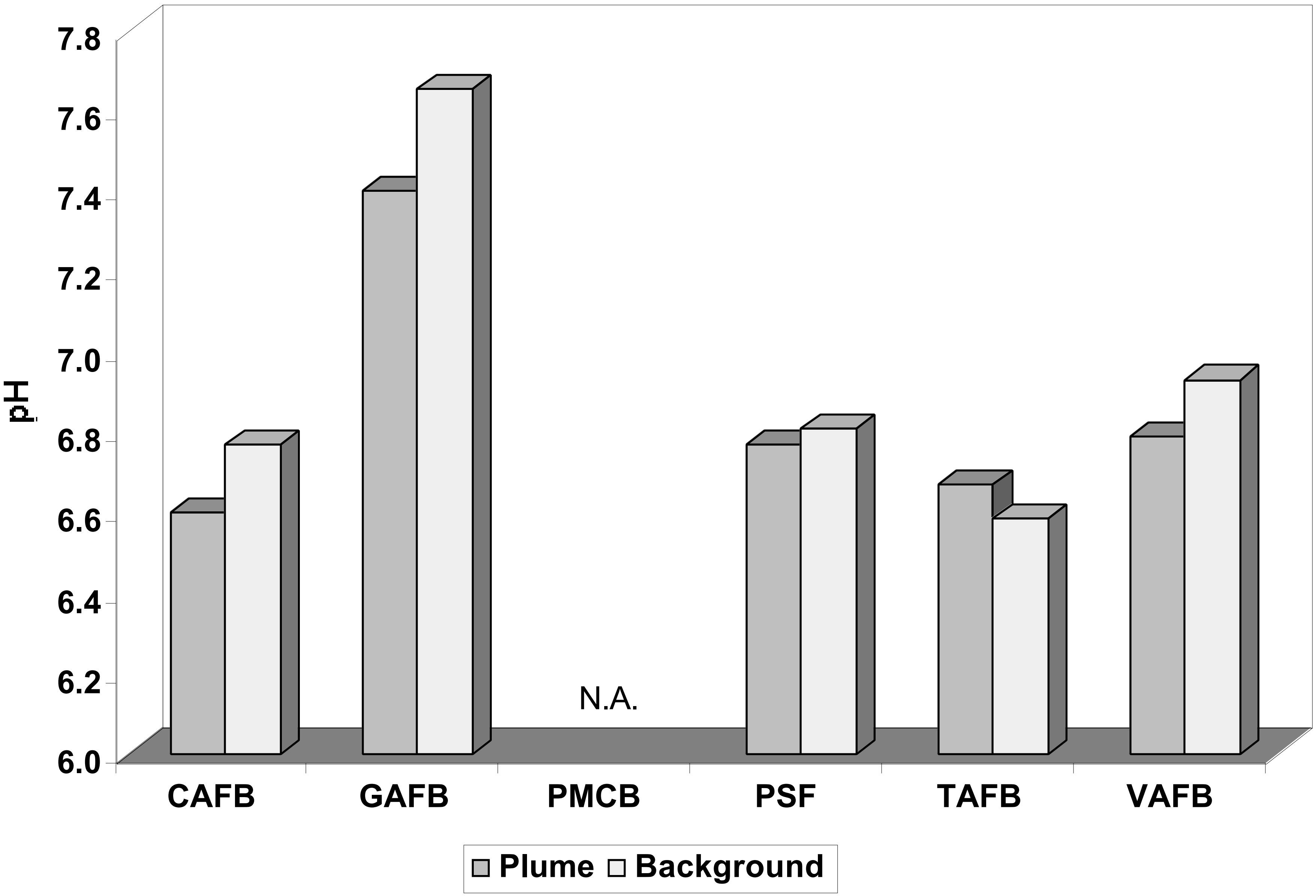

Figure E-1.10. pH: comparison between median values from plume interior wells and median values from background wells.

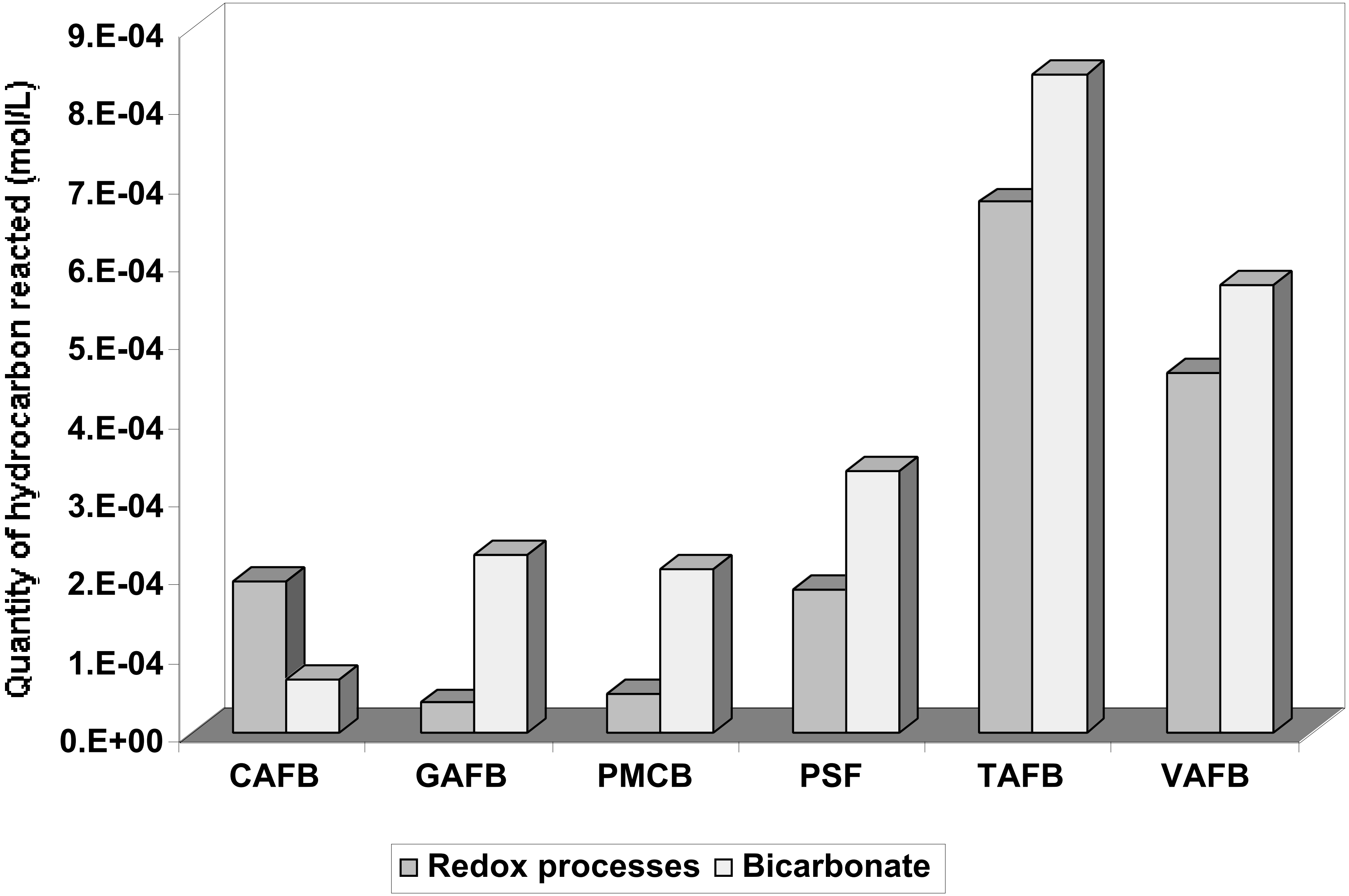

Figure E-1.11. Mass balance comparison of biotransformed fuel hydrocarbon mass implied by analysis of electron acceptor concentration differences and biocarbonate alkalinity.

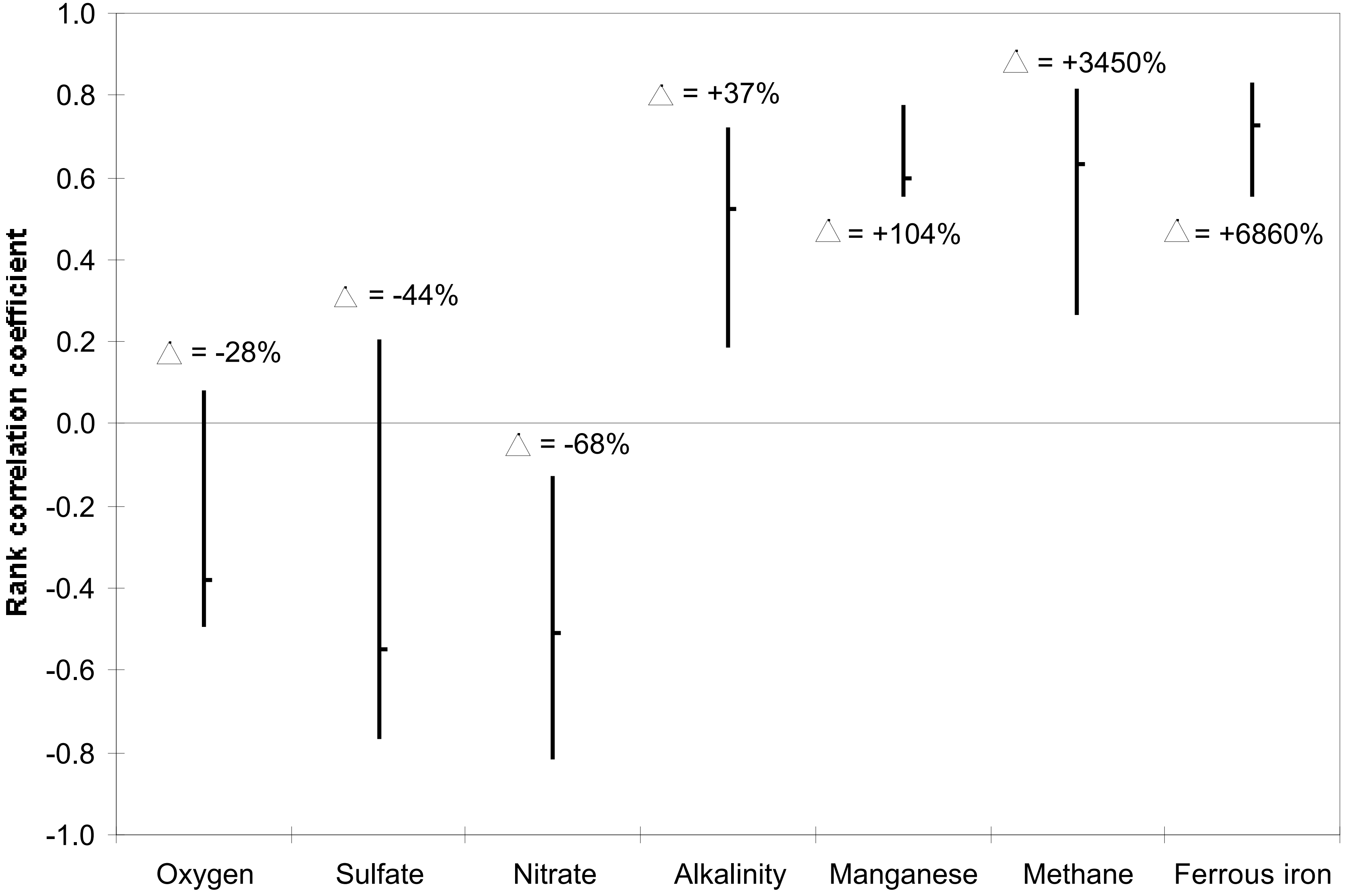

Figure E-1.12. Relationship between correlation coefficient (geochemical indicator value versus hydrocarbon concentration) and indicator signal-to-noise ratio.

Appendix E
Section E-2

Uncertainty Analysis of Fuel Hydrocarbon Biodegradation Signatures in Groundwater by Proabilistic Modeling

Appendix E (Section E-2)

Uncertainty Analyses of Fuel Hydrocarbon Biodegradation Signatures in Ground Water by Probabilistic Modeling

E-2.1. Introduction

Fuel hydrocarbon compounds (FHCs) associated with leaking underground fuel tanks (LUFTs) and pipelines are common ground water contaminants. Aromatic constituents such as benzene, toluene, ethylbenzene, and xylenes (BTEX) are of particular regulatory concern because of their relatively high solubility in water and possible long-term health effects (especially benzene). It is well-recognized that FHCs will biodegrade under a variety of conditions (e.g., Reinhard, Goodman, and Barker, 1984; Barker and others, 1986; Major et al., 1988; Grbic-Galic and Vogel, 1991; Haag et al., 1991; Kazumi et al., 1997). The recent study by Rice et al. (1995) showed that lengths of BTEX plumes in shallow ground water tend to be limited to distances less than approximately 80 meters from the source (based on California data). This finding was supported by Buscheck et al. (1996) as well as by Mace et al. (1997). Natural attenuation mechanisms (i.e., primarily biodegradation) were cited as a probable explanation for plume length limitation.

Regulators, site stakeholders, and the scientific community have begun to recognize that natural attenuation processes can effectively remediate ground water contaminated with FHCs. To assess the risk to potential downgradient receptors, transport models are often used to predict future plume behavior and cleanup time. However, even when employing simple models, uncertainty in ground water velocity, mean contaminant degradation rate, dispersivities, and the nature of the source term (i.e. location, release history, total contaminant mass) create cumulative uncertainties in projected plume behavior. Moreover, because models are calibrated to existing or historical contaminant concentration data, the effect of parameter uncertainty is to produce non-unique solutions to the contaminant transport problem. Thus, to improve practical decision-making processes associated with LUFT sites, uncertainty in model forecasts, and the relationship to parameter uncertainty, must be quantified and analyzed.

The problem of constraining parameter and forecast uncertainty often requires extensive data collection (e.g., installation of numerous monitoring wells) and thus additional costs. However, biodegrading FHCs often measurably affect the local inorganic geochemistry through coupled oxidation-reduction reactions which are mediated by microorganisms in the subsurface (e.g., Lovley et al., 1989; Cozzarelli and Baedecker, 1992; Baedecker et al., 1993; Vroblesky and Chapelle, 1994; Borden et al, 1995; Vroblesky et al., 1996). For example, electron acceptors such as oxygen, nitrate, or sulfate may be locally depleted in association with FHC oxidation, whereas chemically-reduced species (e.g., sulfide, methane) or mineralization products (i.e., carbon dioxide) may accumulate. Because these data are often collected as part of routine ground water sampling activities, they may be used to provide constraints on the relationships between mean degradation rates, source mass, and other factors. The key to using these constraints to reduce uncertainty is to dynamically link geochemical indicator concentration data to the contaminant transport model.

To quantify forecast uncertainties, a probabilistic modeling approach has been developed which links the reactive transport of FHCs to the local geochemistry using superposition of an analytical transport model, reaction stoichiometry, and Monte Carlo simulation. This approach allows uncertainties in hydrogeologic data (e.g., hydraulic conductivity, hydraulic gradient magnitude and direction) and geochemical data (e.g., background electron acceptor concentrations, degradation rates) to be translated into uncertainties regarding forecast contaminant and electron acceptor concentrations at individual wells. Sensitivity analyses of these results can provide insights into the critical data needed for quantifying the behavior of plumes.

E-2.2. Modeling Approach

Wilson and Miller (1978) presented an analytical solution for solute transport in a homogeneous, infinite aquifer of constant thickness with a uniform fluid flow field assuming an instantaneous point source. Modified to account for retardation and a continuous source release, this solution may be written as,

$$c(x,y,t) = \int_{\tau=0}^{\tau=t} \frac{dM}{4\pi\phi\tau H\sqrt{D_l D_t}} \exp\left[-\frac{(x-\frac{v}{R}\tau)^2}{4\frac{D_l}{R}\tau} - \frac{y^2}{4\frac{D_t}{R}\tau} - \lambda\tau \right] d\tau \qquad \text{(E-2-1)}$$

where dM is the mass introduced into the system per unit time, ϕ the porosity, H the aquifer thickness, D_l and D_t the longitudinal and transverse dispersion coefficients, respectively; v the ground water velocity, R the retardation coefficient, λ the first-order decay coefficient, x and y, the distances between the source location and the monitor point in the longitudinal and transverse directions, respectively, and t the elapsed time between source introduction and sampling time. Although Eq. (E-2-1) is a highly idealized conceptualization of solute transport, it does serve as a reasonable probability distribution model of contaminant concentrations in space and time. The uniform first-order kinetic model is a simplifying assumption which neglects the influences of microbial growth on substrate utilization rates. Moreover, it does not account for variability in degradation rates associated with different biogeochemical redox regimes. Nevertheless, as a screening model for engineering decision-making with sparse field data, the first-order kinetic model often serves as a useful first approximation (MacIntyre et al., 1993; Wilson et al., 1995, Buscheck et al., 1996), particularly when redox conditions are largely anaerobic (Rafai et al., 1987)

At a given location (x, y), the cumulative FHC quantity which has undergone biodegradation, ΔC, is given by superposition according to,

$$\Delta c(x,y,t) = \int_{\tau=0}^{\tau=t} \frac{dM}{4\pi\phi\tau H\sqrt{D_l D_t}} \exp\left[-\frac{(x-\frac{v}{R}\tau)^2}{4\frac{D_l}{R}\tau} - \frac{y^2}{4\frac{D_t}{R}\tau} \right] d\tau \; -$$

$$\int_{\tau=0}^{\tau=t} \frac{dM}{4\pi\phi\tau H\sqrt{D_l D_t}} \exp\left[-\frac{(x-\frac{v}{R}\tau)^2}{4\frac{D_l}{R}\tau} - \frac{y^2}{4\frac{D_t}{R}\tau} - \lambda\tau \right] d\tau \tag{E-2-2}$$

Eq. (E-2-2) describes the amount of FHC which has been previously transformed upgradient. Using toluene, C7H8, as a surrogate for the cumulative concentration of FHCs, the oxidation of Δc must be balanced stoichiometrically by the reduction of one or more electron acceptors as given by,

$$\mathrm{C7H8 + 9O2 \rightarrow 7CO2 + 4H2O} \tag{E-2-3}$$

$$\mathrm{C7H8 + 18MnO2 + 36H+ \rightarrow 7CO2 + 18Mn2+ + 22H2O} \tag{E-2-4}$$

$$\mathrm{5C7H8 + 36NO3- + 36H+ \rightarrow 35CO2 + 18N2 + 38H2O} \tag{E-2-5}$$

$$\mathrm{C7H8 + 36Fe(OH)3 + 72H+ \rightarrow 7CO2 + 36Fe2+ + 94H2O} \tag{E-2-6}$$

$$\mathrm{2C7H8 + 9SO42- + 18H+ \rightarrow 14CO2 + 9H2S + 8H2O} \tag{E-2-7}$$

$$\mathrm{2C7H8 + 10H2O \rightarrow 14CO2 + 9CH4} \tag{E-2-8}$$

These reactions are listed by decreasing thermodynamic favorability, a sequence generally followed by microorganisms to obtain the maximum energy benefit. To address this sequence in the model, the quantity of FHC biodegraded at a given point is first calculated by Eq. (E-2-2). Electron acceptor concentrations are then adjusted, in sequence, based Eqs. (E-2-3) through (E-2-8) until all of the mineralized FHC is accounted for in the mass balance. For iron and manganese, the electron acceptor species consist of solid-phase mineral oxides. For modeling purposes, these may be represented as fictitious aqueous species based upon observed concentrations of Fe^{2+} and Mn^{2+} within the hydrocarbon plume. Methane concentrations may be predicted directly using Eq. (E-2-8). Assuming that most of the carbon dioxide produced in the FHC mineralization reactions is converted to bicarbonate under near-neutral pH conditions, local changes in carbon dioxide (bicarbonate) can be estimated by Eqs. (E-2-3) through (E-2-8). At present, the model ignores the conversion of a fraction of the hydrocarbon material into cell biomass.

In cases of significant retardation of FHCs resulting from adsorption, the model is not applicable. This is because the superposition of the analytical model assumes that all constituents are characterized by the same mobility. Thus, any scenarios which assume a retardation coefficient greater than 1.0 for FHCs assume the same retardation for all electron acceptors, methane, and bicarbonate. This may lead to significant error in certain instances.

Probabilistic modeling of dynamic transport involves utilizing user-specified probability distributions of physical and chemical model parameters, representing uncertainty in data, to produce forecasts through multiple Monte Carlo realizations. Monte Carlo analyses are routinely used in engineering probability forecasting applications (Ang and Tang, 1984, Press et al., 1992). Woodbury et al. (1995) discuss the use of Monte Carlo analyses in practical ground water engineering applications. Each Monte Carlo simulation in this study consisted of executing 1,000 realizations within the prescribed parameter space at each monitoring well location and tallying the forecast concentrations. Forecast probabilities were then compared to measured concentrations of each constituent.

All calculations in this study were conducted using commercial spreadsheet software (Decisioneering, Inc., 1996). Eq. (E-2-2) was integrated numerically using the midpoint rule.

E-2.3. Example Application

The model developed in this study was applied to ground water quality data collected from the North-South Gas Station (NSGS) site at Travis Air Force Base in Fairfield, California. The site consists of two gasoline service stations from which unknown quantities of gasoline were released into the subsurface from LUFTs between the 1960s and the late 1980s. Site geology is characterized by unconsolidated Holocene and Pleistocene alluvial clays, silts, sands, and gravels. Ground water is encountered at a depth of approximately 4 to 5 meters below surface under semi-confined conditions. The ground water flow direction is to the south-southeast at a rate of approximately 10-15 m/yr. Monitoring well data indicate a dissolved BTEX plume extending some 100 meters downgradient of the South Gas Station (Parsons Engineering Science, 1996). Differences in geochemical indicator parameter values between BTEX-contaminated and uncontaminated wells are shown on Table E-2.1. Differences in indicator concentrations between plume interior and background strongly suggest that sulfate reduction is the most important biodegradation mechanism at the site, accounting for over 95% of the inferred electron acceptor utilization.

The BTEX plume at the NSGS site, based on August-September, 1995 monitoring well data, is shown on Fig. E-2.1. Two modeled hydrocarbon plume realizations, using the example parameter values listed on Table E-2.2 (based largely on site data), are also shown on the figure. For modeling purposes, BTEX is assumed to represent all of the biodegradable portion of the FHCs; toluene is in turn used as a surrogate for BTEX. Despite the differences in key parameters between the two realizations, both modeled plumes qualitatively resemble the observed distribution. Measured and modeled sulfate and bicarbonate concentration distributions are shown on Figs. E-2.2 and E-2.3, respectively. Again, a general qualitative correlation exists between the field data and the simulated distributions for both realizations. Similar qualitative correlations also exist with respect to the other geochemical indicators (data not shown).

Clearly, within a parameter space constrained by reasonable expectations for hydrogeologic and geochemical variables, a number of potential solutions exist which may reproduce general trends in field observations. Ideally, one approach for reconciling parameter estimates to achieve the best match to all observed data is through non-linear optimization, using Newton-Raphson iteration or some other error-minimization technique. However, such an approach fails to adequately address uncertainties and thus provides no means for quantifying confidence in the results. An alternative approach is to utilize multiple realizations, with parameters chosen from within prescribed probability distributions, to produce ranges of forecast values. Sensitivity of results to model parameters may then be assessed.

For the NSGS site model, transport model parameter assumptions are listed on Table E-2.3, along with background distributions of sulfate and bicarbonate. Background probability distributions for the remaining geochemical indicators (not shown) were also based on fitting monitoring data. These probability distributions reflect limited empirical observations or postulations and do not necessarily represent the true parameter distribution functions, which are unknown. For example, mean hydraulic conductivity probability distributions reflect estimated hydraulic conductivities from a small number of pumping tests and slug tests. As such, only a limited portion of the true distribution of sediment types present in the subsurface is represented, so forecast results must always be treated with the appropriate degree of caution.

Forecast median and measured concentrations of total BTEX, sulfate (the dominant electron acceptor), and bicarbonate (the most widespread indicator of mineralization) are shown on Figs. E-2.4 through E-2.6, respectively. Error bars indicate the forecast confidence intervals delineated by the 25th and 75th percentiles. Measured BTEX concentrations (Fig. E-2.4) in 9 out of 14 wells with detectable BTEX concentrations fall between the 25th and 75th forecast percentiles. Median forecast concentrations exceed measured concentrations to varying degrees in 6 of the 14 wells. Correlation between median forecast values and field data is marginal, with a rank-based correlation coefficient of only 0.51. Forecast BTEX concentrations are also characterized by very high uncertainties. With regard to sulfate (Fig. E-2.5), aside from three outlier wells characterized by very high sulfate concentrations, measured values generally fall within the middle two quartiles (18 out of 25 wells). Median forecast values exceed field data in 16 of 25 wells. Again, the degree of correlation is marginal ($R = 0.40$ by rank correlation) and a high degree of uncertainty exists in the forecasts. Forecast bicarbonate concentrations (Fig. E-2.6) reflect moderate agreement with observations, with measured values falling within the middle two quartiles in 15 out of 28 wells. Median forecast values exceed field data in 15 of 28 wells. The rank-based correlation coefficient between median forecast values and field data is 0.56. Forecasts of other geochemical indicators (dissolved oxygen, nitrate, iron, manganese, methane) are not shown because of the large number of non-detections, either in observation data or in forecast values.

For each of the three parameters, the number of forecast median values which exceed measured concentrations is roughly equal to half of the number of observations, indicating a lack of a strong systematic bias in forecast values. This suggests that the essential parameter ranges chosen do not reflect gross overestimates or underestimates of such factors as source mass or degradation rate. The partial degree of correlation between forecast values and field data also suggests that the model is reflecting the coupled transport and biogeochemical processes occurring at the site to some degree. However, the main feature apparent in the simulation results is the high degree of uncertainty associated with forecast concentrations at any one monitoring location, even within the fairly well-constrained parameter space outlined on Table E-2.3. Thus, the question of which parameters exert the most significant influence on various forecasts emerges as the central issue of this study.

E-2.4. Sensitivity Analyses

Sensitivity analyses provide insight into the impact of parameter probability distributions on uncertainty in forecast variability. To quantify sensitivity, parameters and forecasts are rank-correlated. Rank correlation offers an advantage over normal (value) correlation in that it can address strongly nonlinear trends in the data and can suppress the effects of outliers in skewing the correlation coefficient (Isaaks and Srivastava, 1989). Rank correlation involves assigning ranks to both the dependent variable (the forecast) and the independent variable (the parameter) and performing a linear regression on the corresponding rank sets. The resulting correlation coefficients are then tallied for each forecast and normalized. This yields the relative contribution to variance of each parameter (e.g., hydraulic conductivity, source location, background concentration) to each forecast (concentrations of total BTEX and geochemical indicators at each well).

Parameter sensitivities for forecast BTEX concentrations as a function of distance from the source area are shown on Fig. E-2.7. A variety of factors appear to impact forecast variability in the source area, particularly uncertainty in the degradation rate, source location (southern gas station), and hydraulic conductivity. Further downgradient, uncertainty in the ground water velocity, as indicated by uncertainties in conductivity and gradient, is more important, while factors pertaining to the nature of the source term(s) are less significant. In particular, uncertainty in the degradation rate, perhaps the most significant factor impacting forecasts in the source area, becomes less significant by comparison further downgradient. It must be emphasized that at other sites with different parameter distributions, the contributions to uncertainty will differ from the results observed with respect to this example site.

Parameter sensitivities for selected geochemical indicators in MW-138 and MP-7 (monitor wells in the source vicinity and far downgradient at the NSGS site, respectively) are shown on Table E-2.4. The pattern of parameter sensitivity appears to be more complex in comparison to that of BTEX. For sulfate, uncertainty in the background concentration dominates forecast variance, both near the source area and far downgradient (apparent sensitivity to background bicarbonate results from the prescribed correlation between the two parameters). This reflects the high variability and high concentrations of background sulfate values. In contrast, uncertainties in bicarbonate concentrations primarily reflect uncertainties in other factors (ground water velocity parameters, source location) near the source area in addition to uncertainty in background concentration. This is an indication of the strong influence of FHC mineralization on bicarbonate concentrations near the source area. Further downgradient, uncertainty in the background concentration dominates. Forecast methane levels in the source area are significantly affected by uncertainties in the background sulfate concentration. This is a result of the sequential electron acceptor reaction sequence assumed by the model: Sulfate must be fully exhausted before methanogenesis is assumed to occur. Uncertainty in forecast oxygen levels far downgradient of the plume is dominated by uncertainty in the ground water velocity. Similar patterns are associated with nitrate, iron, and manganese concentrations (not shown). Because of the relatively low concentrations involved, each of these electron acceptors is likely to be entirely utilized in the source area. Thus, changes in concentration in the downgradient direction are in large part a reflection of the migration rate of the anaerobic shadow emerging from the BTEX plume.

Surprisingly, variances in forecast geochemical indicator concentrations do not appear to be sensitive, in a relative sense, to uncertainty in the BTEX degradation rate. In the source area, this is because uncertainty in the background concentrations dominates the forecast concentrations. Downgradient, forecast concentrations are most affected by uncertainty in the ground water velocity, which determines the extent of the geochemical signature migration. Again, it should be noted that at other sites with different parameter distributions, the contributions to uncertainty will differ. This may be especially true with regard to sulfate and bicarbonate, which are characterized by very high background values at the NSGS site.

E-2.5. General Applicability of the Approach

Aside from the specified variability in model parameters, a number of other factors may contribute to the discrepancies between forecast concentrations and field data. These include physical heterogeneities in the flow field not adequately addressed by the dispersion model, transport in the third dimension (including dilution effects associated with long well screens), complex source release history, significant retardation effects, and spatially-variable biodegradation rates. Another potential source of error for the example application is the use of BTEX concentrations (represented by toluene as a surrogate) as a mass balance constraint on geochemical indicator concentrations. In reality, non-BTEX components present in the gasoline mixture will also biodegrade and influence the local geochemistry as well. Nevertheless, given the large uncertainties associated with BTEX concentrations in the existing model (Fig. E-2.4), this effect may be relatively small by comparison at the NSGS site.

Despite these potential shortcomings, this approach presents a reasonable probability distribution model for fuel hydrocarbon and geochemical indicator concentrations in the absence of a more detailed conceptual model. As such, this approach should be applicable to a variety of LUFT sites which have been characterized to a similar degree. Nevertheless, the findings pertaining to the BTEX plume analyses at the NSGS site are site-specific, reflecting a particular hydrogeologic and biogeochemical setting, and may or may not be characteristic of other LUFT cases. This pertains not only to the ranges of forecast concentrations but to parameter sensitivities as well.

The value in applying this technique to LUFT sites is that the uncertainties associated with predictive modeling may be quantified. Biodegradation tends to limit the migration of FHC plumes; the input of dissolved FHCs from residual sources is balanced by losses through biodegradation, integrated over the extent of the plume. Hence, biodegradation can protect downgradient receptors by preventing migration of the plume beyond a certain distance from the source. Variances in concentration forecasts thus translate into uncertainties in receptor impact. This information allows for more informed cleanup decision-making from a regulatory perspective. If uncertainties must be reduced in specific cases, further data collection may be recommended and more detailed modeling attempted. In this way, the extent to which a site must be characterized to develop appropriate engineering solutions may be determined in an objective and systematic manner.

E-2.6. References

Ang, A. H-S., W. H. Tang (1984), "Probability Concepts in Engineering Planning and Design, v. 2: Decision, Risk, and Reliability" (John Wiley & Sons, New York).

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 ground water, *Applied Geochemistry* **8**(6), pp. 569–586.

Barker, J. F., J. S. Tessman, P. E. Plotz, and M. Reinhard (1986), "The organic geochemistry of a sanitary landfill leachate plume," *Journal of Contaminant Hydrology* **1**(1/2), 171–189.

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

Buscheck, 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. Vroblesky (1996), "Measuring rates of biodegradation in a contaminated aquifer using field and laboratory methods," *Ground Water* **34**(4), 691–698.

Cozzarelli, I. M., and M. J. Baedecker (1992), "Oxidation of hydrocarbons coupled to reduction of inorganic species in ground water," in *Water-Rock Interactions*," Y. K. Kharaka, and A. S. Maest, and A. A. Balkema, Eds. (Rotterdam, Netherlands), pp. 275–278.

Decisioneering, Inc. (1996), "Crystal Ball: Forecasting and Risk Analysis for Spreadsheet Users," Decisioneering, Inc., Aurora, Colorado.

Grbic-Galic, D., and T. M. Vogel. (1987), "Transformation of toluene and benzene by mixed methanogenic cultures," *Applied and Environmental Microbiology* **53**(2), 254–260.

Haag, F., M. Reinhard, and P. L. McCarty (1991), "Degradation of toluene and p-xylene" in *Anaerobic microcosms: Evidence for sulfate as a terminal electron acceptor*, Environmental Toxicology and Chemistry **10**(11), 1379–1390.

Isaaks, E. H., and R. M. Srivastava (1989), "An Introduction to Applied Geostatistics" (Oxford University Press, Oxford, England).

Kazumi, J., M. E. Caldwell, J. M. Suflita, D. R. Lovley, and L. Y. Young (1997), "Anaerobic degradation of benzene in diverse anoxic environments," *Environmental Science and Technology* **31**(3), 813–818.

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.

Mace, R. E., R. S. Fisher, D. M. Welch, and S. P. Parra (1997), "Extent, Mass, and Duration of Hydrocarbon Petroleum Storage Tank Sites in Texas" *Bureau of Economic Geology*, University of Texas at Austin.

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**(12), 4045–4051.

Major, D. W., C. I. Mayfield, and J. F. Barker (1988), "Biotransformation of benzene by denitrification in aquifer sand," *Ground Water* **26**(1), 8–14.

Parsons Engineering Science (1996), "Final Treatability Study to Evaluate Intrinsic Remediation at the North and South Gas Stations," Travis Air Force Base, California, Prepared for the Air Force Center for Environmental Excellence, Brooks Air Force Base, Texas.

Press, W. H., S. A. Teukolsky, W. T. Vetterling, B. P. Flannery (1992), "Numerical Recipes in FORTRAN," (2nd Edition) (Cambridge University Press, New York).

Rafai, H. S., P. B. Bedient, J. T. Wilson, K. M. Miller, and J. M. Armstrong (1987), "Biodegradation modeling at aviation fuel spill site," *Journal of Environmental Engineering, American Society of Civil Engineers* **114**(5), 1007–1029.

Reinhard, M., N. L. Goodman, and J.F. Barker (1984), "Occurrence and distribution of organic chemicals in two landfill leachate plumes," *Environmental Science and Technology* **18**(12), 953–961.

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. Chapelle (1996), "Influence of electron donor on the minimum sulfate concentration required for sulfate reduction in a petroleum hydrocarbon-contaminated aquifer," *Environmental Science and Technology* **30**(4), 1377–1381.

Wilson, J. L., and P. G. Miller (1978), "Two-dimensional plume in uniform ground-water flow," Journal of the Hydraulics Division, in *Proceedings of the American Society of Civil Engineers* **104**(4), 503–514.

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*, Hinchee, R.E., J. T. Wilson, and D.C. Downey, Eds. (Battelle Press, Richland, Washington), pp. 91–100.

Woodbury, A., F. Render, and T. Ulrych (1995), "Practical probabilistic groundwater modeling," *Ground Water* **33**(4), 532–538.

Table E-2.1. Median geochemical indicator concentrations in background wells (BTEX not detected) and plume interior wells (BTEX present above detection limit).

Indicator	Background (mg/L)	Plume interior (mg/L)
O_2	0.5	0.2
Fe(II)	0.03	2.8
Mn^{2+}	0.1	2.8
NO_3^-	4.9	0.95
SO_4^{2-}	876	530
CH_4	0.0045	0.16
HCO_3^-	393	746

Table E-2.2. Parameter values for two model realizations of the NSGS plume.

Parameter	Realization #1	Realization #2
Total mass per gas station (liters of gasoline)	**103,700**	**51,800**
Total mass per gas station[*], M (grams of BTEX)	**8.30×10^6**	**4.15×10^6**
Length of release period, t (years)	**20**	**20**
First-order degradation rate, λ (day^{-1})	**0.2%**	**0.05%**
Hydraulic conductivity[†] (m/day)	**4**	**4**
Hydraulic gradient magnitude	**0.002**	**0.002**
Gradient direction (degrees)	**295**	**295**
Effective porosity[‡], ϕ	**0.2**	**0.2**
Soil organic carbon[§] (mg/Kg)	**1,600**	**1,600**
Soil bulk density, ρ_b (g/cm^3)	**1.65**	**1.65**
Aquifer thickness, H (m)	**3**	**3**
Ratio of α_l to plume length scale[**]	**0.1**	**0.05**

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[*] Assuming BTEX volume is equal to 10% of total gasoline volume; BTEX density = 0.8 g/cm^3. M is introduced at a uniform rate into the system over the time period t.

[†] Velocity, v, used in Eq. (2) calculated from Darcy's law and porosity value.

[‡] Total porosity is assumed to be equal to 1.5 times the effective porosity for calculation of the retardation coefficient.

[§] Retardation coefficient, R, used in Eq. (2) calculated from the relationship $R = 1 + K_{oc}f_{oc}\rho_b/\phi$, where f_{oc} is the fractional organic carbon content of the sediments and K_{oc}, the organic carbon partitioning coefficient, is assumed to be equal to 280 ml/g as a representative value for BTEX.

[**] Dispersion coefficients, D_l and D_t, calculated by $D_l = v\alpha_l$ and $D_t = v\alpha_t$, where α_l and α_t are the longitudinal and transverse dispersivities, respectively. Plume length scale is given by *vt*.

Table E-2.2. (Continued)

Parameter	Realization #1	Realization #2
Ratio of α_t to α_l	**0.1**	**0.025**
Background SO_4^{2-} (mg/L)	**876**	**876**
Background HCO_3^- (mg/L)	**390**	**390**

Table E-2.3. Probability distributions of transport parameters used in Monte Carlo model.

Parameter	Distribution[*]	Rationale
Total mass per gas station (liters of gasoline)	**Lognormal distribution.** 5% = 51,850 95% = 207,400 Median = 73,100	**Postulated.**
Source locations, both gas stations (m)	**Normal distribution.** Tank location ± 7.6 (N/S and E/W)	**Postulated (accounting for leaks in piping systems, free product pools).**
Release period, t (years)	**Normal distribution; 20 ± 2.**	**Based on tank use history.**
First-order degradation rate, λ (day^{-1})	**Lognormal distribution.** 5% = 0.05% 95% = 1.0% Median = 0.2%	**Postulated, based on reported values for mean degradation rates at other LUFT sites (e.g., MacIntyre et al., 1993, Wilson et al., 1995, Buscheck et al., 1996, Chapelle et al., 1996).**
Hydraulic conductivity (m/day)	**Lognormal distribution.** 5% = 1 95% = 10 Median = 3.2	**Based on site aquifer test data.**
Hydraulic gradient	**Lognormal distribution.** 5% = 0.001 95% = 0.004 Median = 0.002	**Based on a distribution of gradients obtained from trios of site wells.**
Gradient direction (degrees)	**Normal distribution; 295 ± 10.**	**Based on observed spatial variability in NSGS gradient direction.**
Effective porosity, ϕ	**Normal distribution; 0.2 ± 0.02.**	**Postulated.**
Soil organic carbon (mg/Kg)	**Weibull distribution.** Loc = 367 Scale = 693 Shape = 1.36	**Best-fit probability function to analyses of NSGS soil samples.**
Bulk density, ρ_b (g/cm^3)	**Normal distribution; 1.65 ± 0.02.**	**Postulated.**
Aquifer thickness, H (m)	**Normal distribution; 10 ± 1.**	**Based on site data.**
Ratio of α_l to plume length scale	**Lognormal distribution.** 5% = 0.03 95% = 0.33 Median = 0.1	**Postulated.**
Ratio of α_t to α_l	**Lognormal distribution.**	**Postulated.**

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[*] Uncertainty indicated in normal probability distributions refers to standard deviation.

Table E-2.3. (Continued)

Parameter	Distribution*	Rationale
	5% = 0.03 **95% = 0.33** **Median = 0.1**	
SO_4^{2-}	**Exponential distribution.** **Rate = 7.19×10^{-4}**	**Best-fit probability function. Correlated with alkalinity by analysis of monitoring well data (R = 0.67).**
Alkalinity[†]	**Lognormal distribution.** **5% = 106** **95% = 872** **Median = 304**	**Best-fit probability function. Correlated with SO_4^{2-}.**

[†] Measured alkalinity values converted to HCO_3^- to model reaction stoichiometry.

Table E-2.4. Sensitivity of select forecast geochemical indicator concentrations to model parameters.

	SO42-		Bicarbonate		CH4	O2
Parameter well	**MW-138**	**MP-7**	**MW-138**	**MP-7**	**MW-138**	**MP-7**
Background SO42-	**54%**	**69%**	**5%**	**29%**	**31%**	**<1%**
Background HCO3-	**22%**	**30%**	**18%**	**67%**	**13%**	**<1%**
Total mass per gas station	**5%**	**<1%**	**8%**	**<1%**	**8%**	**<1%**
Easting (South Gas Station source)	**5%**	**<1%**	**27%**	**<1%**	**17%**	**<1%**
Hydraulic conductivity	**4%**	**<1%**	**14%**	**1%**	**9%**	**51%**
Hydraulic gradient direction	**2%**	**<1%**	**11%**	**<1%**	**6%**	**<1%**
Ratio of t to l	**2%**	**<1%**	**2%**	**<1%**	**3%**	**<1%**
Hydraulic gradient magnitude	**2%**	**<1%**	**3%**	**<1%**	**3%**	**14%**
Northing (South Gas Station source)	**1%**	**<1%**	**4%**	**<1%**	**3%**	**<1%**
Ratio of l to plume length scale	**1%**	**<1%**	**1%**	**<1%**	**1%**	**7%**
Length of release period (time)	**1%**	**<1%**	**1%**	**<1%**	**2%**	**<1%**
Soil organic carbon	**<1%**	**<1%**	**1%**	**<1%**	**1%**	**5%**
First-order degradation rate	**<1%**	**<1%**	**1%**	**<1%**	**<1%**	**<1%**
Background dissolved O2	**<1%**	**<1%**	**<1%**	**<1%**	**<1%**	**20%**
Porosity	**<1%**	**<1%**	**1%**	**1%**	**<1%**	**1%**
Aquifer thickness	**<1%**	**<1%**	**1%**	**<1%**	**1%**	**<1%**
Others	**1.50%**	**1%**	**2%**	**1%**	**1%**	**1%**

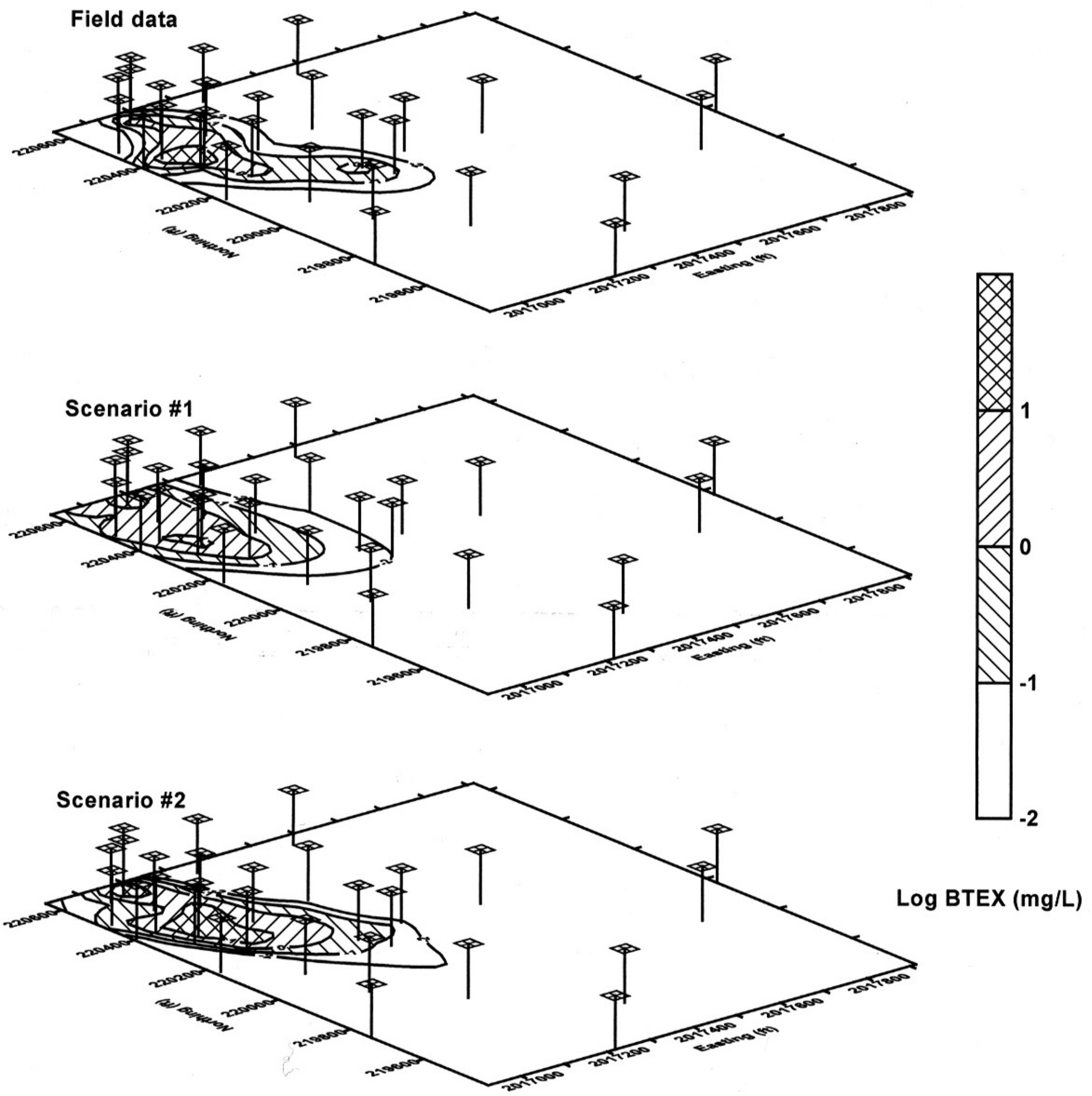

Fig. E-2.1. BTEX plume at the NSGS site (1995); field data (top), simulated Realization #1 (middle), and simulated Realization #2 (bottom). Units are logarithm of concentration (mg/L), contoured by monitoring well locations (hatched squares).

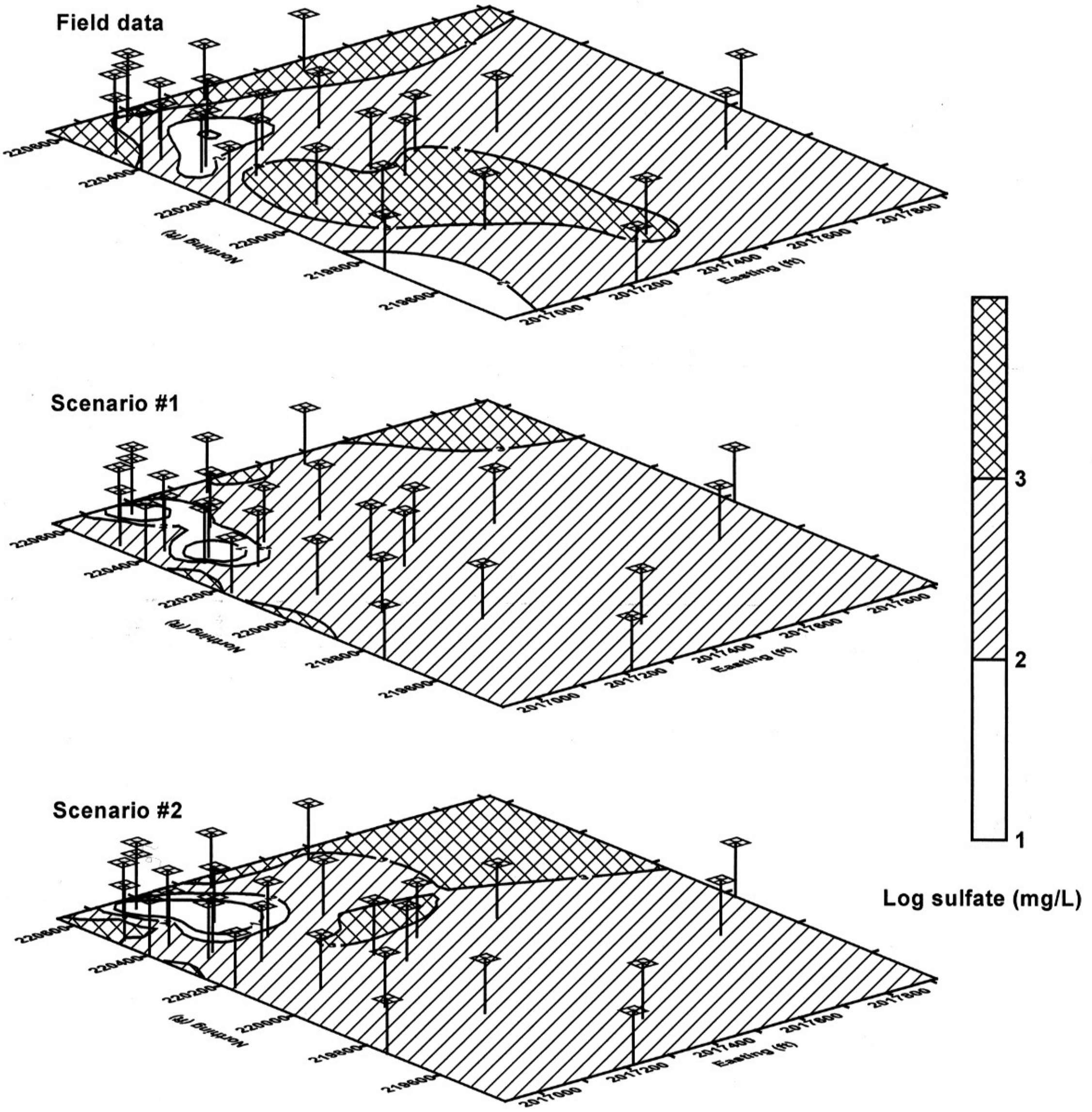

Fig. E-2.2. Distribution of sulfate in ground water at the NSGS site (1995); field data (top), simulated Realization #1 (middle), and simulated Realization #2 (bottom). Units are logarithm of concentration (mg/L), contoured by monitoring well locations (hatched squares).

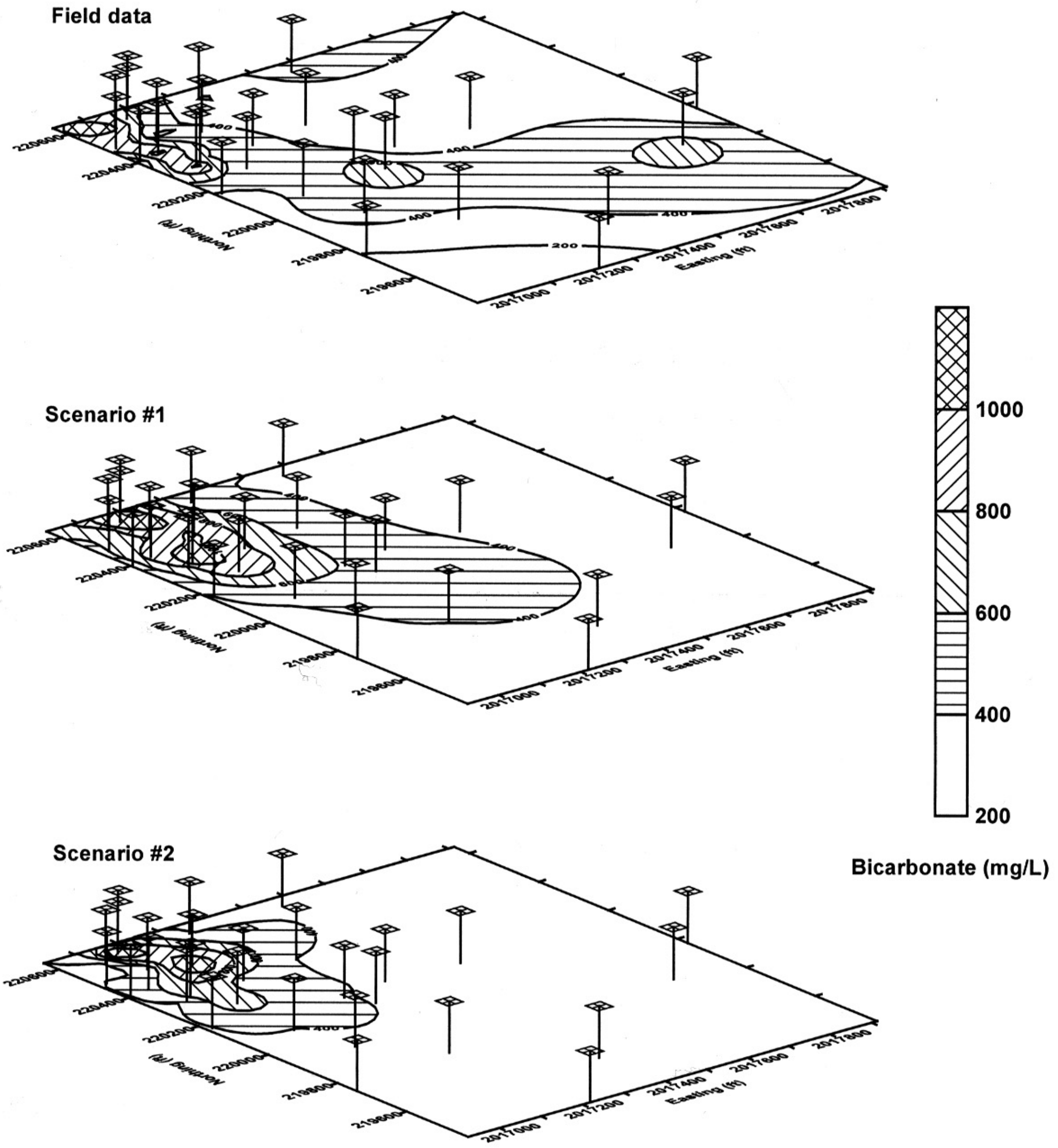

Fig. E-2.3. Distribution of bicarbonate in ground water at the NSGS site (1995); field data (top), simulated Realization #1 (middle), and simulated Realization #2 (bottom). Concentration units are mg/L, contoured by monitoring well locations (hatched squares).

Appendix E
Section E-3

A Critique of a Steady-State Analytical Method for Estimating Contaminant Degradation Rates

Appendix E (Section E-3)

A Critique of a Steady-State Analytical Method for Estimating Contaminant Degradation Rates

E-3.1. Introduction

Fuel hydrocarbons and other common organic contaminants are frequently subject to biotransformation processes in groundwater environments. If the rate of biotransformation of a given contaminant at a site is assumed to be uniform in time and space, then in the presence of a continuous source (e.g., a residual pool of free product), the plume associated with the dissolved contaminant will achieve a steady-state configuration. This occurs as a result of a mass balance between contaminant influx from the source (e.g., free-product dissolution) and contaminant loss through biotransformation reactions integrated across the spatial extent of the plume. Therefore, the contaminant biotransformation rate will play a major role in determining the spatial extent of a steady-state contaminant plume in the direction downgradient from the source.

Buscheck and Alcantar (1995) suggested that the steady-state distribution of contaminant concentrations downgradient of a continuous source can be used to estimate transformation rates. This rate information is very useful, for example, in the assessment of the transport of a contaminant between its source and a risk receptor and in determining the required corrective action. Assuming a first-order decay coefficient as an approximation for the biotransformation of the contaminant, Buscheck and Alcantar (1995) showed, for a one-dimensional idealization, that the degradation rate λ may be given by,

$$\lambda = \frac{v_c}{4\alpha_x}\left(\left[1 + 2\alpha_x\left(\frac{k}{v_x}\right)\right]^2 - 1\right) \tag{E-3-1}$$

where v_c is the contaminant velocity along the x-direction (adjusted for retardation), α_x the longitudinal dispersivity, k the overall attenuation rate (units of % time^{-1}), and v_x the groundwater linear velocity. The term k/v_x reflects the slope of a regression line fit to log contaminant concentration data as a function of distance along the plume centerline (units of length^{-1}). This technique is routinely used to estimate biotransformation rates of contaminants in groundwater (e.g., Ellis, 1996; Brown et al., 1997; Herrington et al., 1997; Westervelt et al., 1997). However, it must be recognized that a significant potential for misinterpretation of results exists in applying this method. Buscheck and Alcantar (1995) intended for the method to be an idealization, recognizing that additional work and investigation would be required in order to narrow the bounds of the probable degradation rates. The difficulty arises when dispersive processes (macroscale mechanical mixing and molecular diffusion) produce concentration distributions which, ideally, decline with distance from a continuous source as determined by an error function term (even in the absence of any solute degradation). In many instances, particularly when analyzing only a small number of data points (i.e. monitoring wells), it is often possible to fit a straight line through log concentration versus distance data with a high degree of correlation even when biotransformation is insignificant or absent altogether. Therefore, it is possible to derive estimated biotransformation rates which are entirely spurious.

E-3.2. Analyses

E.3.2.1. Potential for Misapplication to Non-Transforming Contaminants

The method of Buscheck and Alcantar (1995) constitutes an inverse solution technique. Inverse solutions by their nature are particularly sensitive to the initial and boundary conditions associated with the problem. This sensitivity is increased through measurement and modeling errors. Mathematically, such problems are considered ill-posed due to a lack of uniqueness and stability resulting from small changes in the input data. The potential for misinterpretation of the inverse problem through application of the Buscheck and Alcantar (1995) method is best illustrated by an example problem. Consider the total BTEX (benzene/toluene/ethylbenzene/xylene) concentrations measured in three monitoring wells located downgradient of a leaking underground fuel tank (LUFT) site in northern California which is under consideration for remediation by natural attenuation (Table E-3.1). Mean hydraulic conductivity in monitoring wells across the site, estimated from slug tests and pumping tests, is approximately 3.6 m/day. Assuming a hydraulic gradient of 0.002, an effective porosity of 0.25, and a retardation coefficient of approximately 2.0 (based on soil organic carbon content and organic carbon partitioning properties of BTEX), a retarded contaminant velocity of approximately 5.2 m/year may be estimated. Given the length of the BTEX plume at the site, approximately 150 meters based on the 10 μg/L contour, longitudinal dispersivity (characteristic length) may be estimated from the relationship given by Neumann and Zhang (1990),

$$\alpha_x = 0.32L^{0.83} \tag{E-3-2}$$

where L is the scale of the plume length, or simply by assuming a characteristic length equal to 0.10 of the plume length (20 m or 15 m, respectively). Linear regression of log BTEX concentrations as a function of distance from the source area yields a k/v_x value of 0.023, with $R^2 = 0.974$ (Fig. E-3.1). Substitution of this k/v_x value in Eq. (E-3-1) yields biotransformations rate estimates of 0.048% day^{-1} and 0.045% day^{-1} for the Neumann and Zhang and 0.10L dispersion relationships, respectively.

Now consider an alternate scenario. Suppose that the BTEX plume at the site behaves ideally and may be modeled using the familiar Domenico (1987) solution to the two-dimensional advective-dispersive transport equation with a continuous line source,

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

$$\bullet\ \mathrm{erfc}\left[\frac{x-\frac{v}{R}t\left(1+4R\lambda\alpha_x/v\right)^{1/2}}{2\left(\alpha_x\frac{v}{R}t\right)^{1/2}}\right]\bullet\left\{\mathrm{erf}\left[\frac{\left(y+Y/2\right)}{2\left(\alpha_y x\right)^{1/2}}\right]-\mathrm{erf}\left[\frac{\left(y-Y/2\right)}{2\left(\alpha_y x\right)^{1/2}}\right]\right\} \qquad \text{(E-3-3)}$$

Here, C_0 refers to the source concentration (constant with time), α_y the transverse dispersivity, v the groundwater pore velocity, R the retardation coefficient, Y the width of the line source, t the monitor time, and x and y the Cartesian coordinates of the monitor point relative to the source. Assuming a value of 67,000 µg/l for C_0, a source width of 15 m, a flow velocity of 10.4 m/year (corresponding to a contaminant velocity of 5.2 m/year when R = 2.0), and a non-transforming tracer ($\lambda = 0.0$), modeled concentrations as a function of distance may be generated for a variety of longitudinal and transverse dispersivity combinations (Figs. E-3.2 and E-3.3). Given that the Domenico (1987) relationship constitutes a mathematical physical model of solute transport processes, the forecast observations are entirely plausible in that they could, in principle, depict the behavior of a real plume to an observer. For all scenarios chosen, the modeled results resemble the field observations in that log concentration apparently varies linearly with distance from the source. As a result, entirely spurious biotransformation rates can be calculated from Eq. (E-3-1) in the absence of any corroborating information (Table E-3.2), with the highest implied rates corresponding to smaller values of α_x and larger values of α_y.

This example illustrates the potential for misinterpretation of contaminant degradation by the Buscheck and Alcantar (1995) method even under ideal conditions. A linear trend in log concentration values as a function of distance from the contaminant source does not constitute proof of the existence of transformation processes. In particular, it should also be recognized that utilizing only a small number of monitoring wells increases the chances for misinterpretation because of the high probability of a spurious linear fit. For example, consider the results of the example scenario using 11 equidistant monitoring wells instead of three (Fig. E-3.4). The higher well density illustrates a departure from linearity in the log concentration versus distance relationship which was not observed when fewer wells were analyzed.

In reality, many other factors will distort observed concentration profiles in comparison to those predicted by idealized models. A partial list includes (1) the assumption of steady-state conditions where none exist, (2) fluctuations in source strength with time, (3) non-Fickian dispersion of solutes, (4) strongly heterogeneous flow and transport, (5) placement of wells off plume centerline, (6) dilution effects due to well screen length, and (7) non-uniform degradation rate distribution. Thus, fitting concentration data with an exponential function is perhaps simply a matter of chance in many situations, particularly when few monitoring points are utilized, and thus may provide little real insight into transformation processes.

E-3.3. Sensitivity Analyses

Sensitivity analyses provide a means for assessing which parameters exert the greatest influence on the results of the Buscheck and Alcantar method. One approach at addressing the sensitivity issue is to again utilize an idealized model such as the Domenico solution to generate a large number of synthetic BTEX plumes through Monte Carlo simulation, using a range of physical parameter values and biotransformation rates. Monte Carlo simulation is a method by which numbers are randomly drawn from a prescribed series of distributions. The use of Monte Carlo simulations combined with analytical methods results in an output that places confidence limits on the idealized model that can then be compared to the results of a real world situation (e.g., McNab and Dooher, 1998). A comparison of prescribed biotransformation rates in the input parameter probability distribution with inferred rates yielded by application of the Buscheck and Alcantar method to each realization may provide insight into the resulting error distribution. Sensitivity of this error distribution to the parameter input values may offer clues as to which situations are most amenable to the Buscheck and Alcantar method and which are less appropriate.

Hypothesized probability distributions for parameters which directly or indirectly feed into the Domenico relationship (Eq. E-3-3) are shown on Table E-3.3, again with reference to the northern California LUFT site (i.e., with three monitoring points). A total of 1000 realizations were conducted as part of the Monte Carlo simulation. Input for each realization consisted of model parameters chosen randomly in accordance with the probability distributions. Output consisted of forecast concentrations of total BTEX at the three monitoring points (Table E-3.1). Linear regression was performed on the log BTEX concentration versus distance output to produce k/v_x values for input into the Buscheck and Alcantar equation.

Monte Carlo realizations were performed using commercial spreadsheet software. The correlation coefficient relating log total BTEX concentrations and distance was greater than 0.97 in 90% of the realizations, indicating that the Buscheck and Alcantar approach could be applied, in principle, to the vast majority of the cases. Forecast probability (cumulative) distributions of prescribed biotransformation rates as well as the rates derived from the Buscheck and Alcantar approach are illustrated on Fig. E-3.5. These results suggest a significant potential for systematic overestimation of biotransformation rates. This is not surprising, given that the contribution of dispersion in influencing the longitudinal profile of the plume.

A measure of the biotransformation rate estimation error, on a per realization basis, may be given as,

$$\text{Error} = (\lambda_{\text{prescribed}} - \lambda_{\text{B-A}})^2 \qquad \text{(E-3-4)}$$

where $\lambda_{\text{prescribed}}$ refers to the specified bioattenuation rate and $\lambda_{\text{B-A}}$ the bioattenuation rate derived from application of the Buscheck and Alcantar technique. Sensitivity analysis of this defined error function to the input parameters was calculated by rank correlation to avoid the skewing effects of nonlinear relationships between model input and output. The resulting correlation coefficients are shown on Fig. E-3.6. Elapsed time since the initiation of the source appears to be the most significant factor influencing the accuracy of the Buscheck and Alcantar method in this example, with the negative correlation coefficient (R = -0.79) suggesting the greatest error at earliest in the plume history. This is to be expected, as the plume profile will not have had time to stabilize during its initial stages because of the time required for degrading plumes to reach their maximum extent and the rapid growth associated with young plumes. Of secondary influence is the variability associated with dispersion, the velocity-based components of gradient and hydraulic conductivity, and the source width. Thus, the fall-off in concentration with distance is entirely associated with source descriptions and physical transport processes. It is not surprising then that the variability associated with terms that are very uncertain or sparsely sampled to begin with can have significant impact on how degradation rates are developed (Dooher, 1998).

The estimation error also correlates with the value of the derived biotransformation rate (not shown), with a correlation coefficient of +0.73. This suggests that the highest derived biotransformation rates yielded by the Buscheck and Alcantar analyses are the most strongly reflective of non-transformative processes.

E-3.4. Conclusions

The analyses presented in this study suggest that the Buscheck and Alcantar (1995) method for estimating *in situ* biotransformation rates may yield misleading results if not applied in a judicious manner. Buscheck and Alcantar were aware of the possible difficulties, but uncritical application of the method by many workers to groundwater contamination problems continues. Potential erroneous or even spurious transformation rates may arise because of the effects of dispersion in stable plumes as well as in plumes in early stages of development before steady-state is reached. In particular, the method may yield incorrect results when only a small number of wells are used, as the exponential regression will provide a better fit under such circumstances.

These findings imply that biotransformation rates yielded by the Buscheck and Alcantar method should always be substantiated. In principle, this should require that a sufficient number of monitoring wells should be chosen so that the linearity of the log concentration versus distance relationship be either established or refuted. However, in many instances a sufficient number of monitoring wells may be lacking. In such cases, independent means of quantifying transformation rates should be brought to bear. These may include alternate modeling tools such as more comprehensive analytical solute transport models (e.g., Cleary and Ungs, 1978; Wilson and Miller, 1978; Domenico, 1987) or numerical approaches as warranted (Rafai et al., 1987). In addition, mass balance constraints implied by geochemical indicator parameters, such as dissolved oxygen, nitrate, sulfate, iron, bicarbonate, and methane may also providing supporting insights.

E-3.5. References

Buscheck, T. E., and C. M. Alcantar (1995), "Regressive techniques and analytical solutions to demonstrate intrinsic bioremediation," in *Intrinsic Bioremediation,* R. E. Hinchee, J. T. Wilson, and D. Downey, Eds. (Battelle Press, Columbus, Ohio) pp. 109–116.

Brown, K, P. Sererka, M. Thomas, T. Perina, L. Tyner, and B. Sommer (1997), "Natural attenuation of Jet-Fuel Impacted Groundwater," in *In Situ and On-Site Bioremediation: Volume 1, Fourth International in Situ and On-Site Bioremediation Symposium*, New Orleans, April 28–May 1, pp. 83–88.

Chapelle, F. H., P. M. Bradley, D. R. Lovley, and D. A. Vroblesky (1996), "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," Report 78-WR-15, Water Resources Program, Princeton University, Princeton, New Jersey.

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

Dooher, B. P. (1998), "Making risk-based decisions at fuel hydrocarbon impacted sites under sparse data conditions," Ph.D. Dissertation, University of Calif., Los Angeles.

Ellis, D. E, (1996), "Intrinsic remediation in the industrial marketplace," in *Symposium on Natural Attenuation of Chlorinated Organics in Ground Water*, Dallas, Texas, September 11–13, (EPA/540/R-96/509), pp. 120–123.

Herrington, R. T., L. Benson, D. Downey, and J. Hansen (1997), "Validation of fuel hydrocarbon attenuation in low-temperature groundwater environments," in *In Situ and On-Site Bioremediation: Volume 1, Fourth International in Situ and On-Site Bioremediation Symposium*, New Orleans, April 28–May 1, pp. 303–308.

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.

McNab, W. W., Jr., and B. P. Dooher (1998), "Uncertainty analyses of fuel hydrocarbon biodegradation signatures in ground water by probabilistic modeling," *Ground Water*, **36**(4), 691–698.

Neumann, S. P., and Y.-K.Zhang (1990), "A quasi-linear theory of non-Fickian and Fickian subsurface dispersion **1**, Theoretical analysis with application to isotropic media," *Water Resources Research* **26**(5), 887–902.

Rafai, H. S., P. B. Bedient, J. T. Wilson, K. M. Miller, and J. M. Armstrong (1987), "Biodegradation modeling at aviation fuel spill site," *Journal of Environmental Engineering*, American Society of Civil Engineers **114**(5), 1007–1029.

Wilson, J. L., and P. G. Miller (1978), "Two-dimensional plume in uniform ground-water flow," *Journal of the Hydraulics Division*, in *Proceedings of the American Society of Civil Engineers* **104**, pp. 503–514.

Westervelt, W. W., P. W. Lawson, M. N. Wallace, and C. Fosbrook (1997), "Intrinsic remediation of artic diesel fuel near drinking water wells," in *In Situ and On-Site Bioremediation: Volume 1, Fourth International In Situ and On-Site Bioremediation Symposium*, New Orleans, April 28–May 1, pp. 61–66.

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*, Hinchee, R. E., J. T. Wilson, and D. C. Downey, Eds. (Battelle Press, Richland, Washington), pp. 91–100.

Table E-3.1. BTEX concentrations as a function of distance from source.

Well	Distance downgradient (m)	Total BTEX (μg/l)
Well #1	0	67,000
Well #2	26	23,500
Well #3	113	4,095

Table E-3.2. Inferred biotransformation rates from analysis of BTEX concentrations idealized by the Domenico (1987) model.

α_x (m)	α_y (m)	R^2	k/v_x (m^{-1})	Inferred λ (day^{-1})
5	1	0.9845	0.0342	0.058%
10	1	0.9938	0.0263	0.048%
15	1	0.9975	0.0231	0.045%
20	1	0.9991	0.0212	0.043%
5	2.5	0.9975	0.0373	0.064%
10	2.5	0.9999	0.0294	0.055%
15	2.5	0.9976	0.0261	0.052%
20	2.5	0.9945	0.0243	0.052%

Table E-3.3. Probability distributions of parameters used in Monte Carlo model.

Parameter	Distribution	Rationale
Width of source (m)	**Lognormal distribution.** **5% = 1** **95% = 25** **Median = 5**	**Postulated.**
Length of release period, t (days)	**Lognormal distribution.** **5% = 1000** **95% = 10,000** **Median = 3150**	**Postulated.**
First-order degradation rate, λ (day^{-1})	**Lognormal distribution.** **5% = 0.05%** **95% = 1.0%** **Median = 0.2%**	**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, Chapelle et al., 1996).**
Hydraulic conductivity[1] (m/day)	**Lognormal distribution.** **5% = 1** **95% = 10** **Median = 3.2**	**Based on site data (slug tests, aquifer tests).**
Hydraulic gradient magnitude	**Lognormal distribution.** **5% = 0.001** **95% = 0.004** **Median = 0.002**	**Based on spatial variability in gradients observed at the site.**
Porosity, ϕ	**Normal distribution.** **0.25 ± 0.02**	**Postulated.**
Retardation coefficient, R	**Lognormal distribution.** **5% = 1.5** **95% = 5** **Median = 2.7**	**Postulated.**
Longitudinal dispersivity, α_x (m)	**Lognormal distribution.** **5% = 2** **95% = 30** **Median = 7.7**	**Postulated.**
Transverse dispersivity, α_y (m)	**Lognormal distribution.** **5% = 0.2** **95% = 3.0** **Median = 0.8**	**Postulated.**

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[1] Velocity term in the Domenico (1987) relationship estimated by application of Darcy's law to the prescribed hydraulic conductivity, gradient, and porosity.

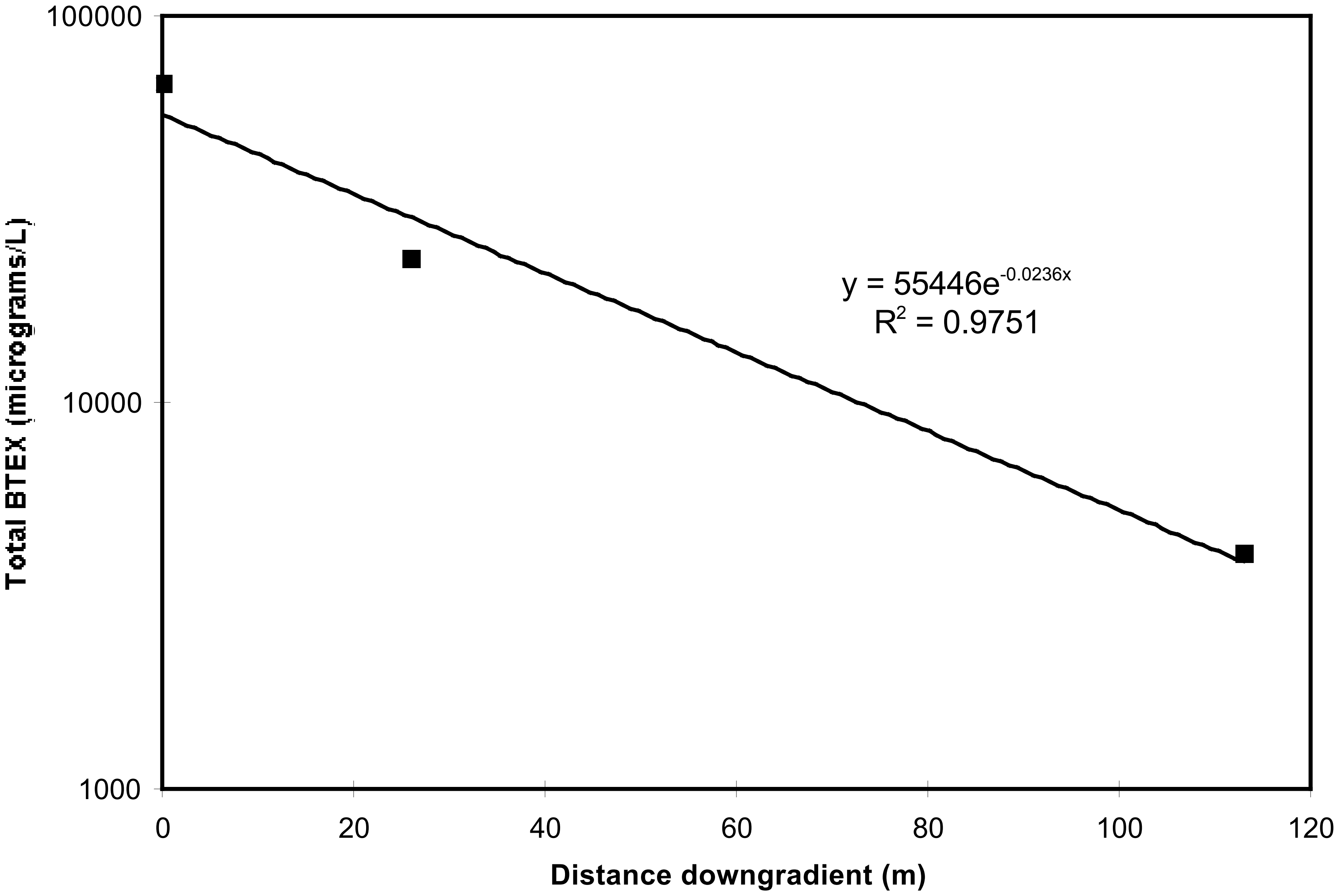

Figure E-3.1. Concentration versus distance downgradient (site data) used in analysis by the method of Buscheck and Alcantar (1995).

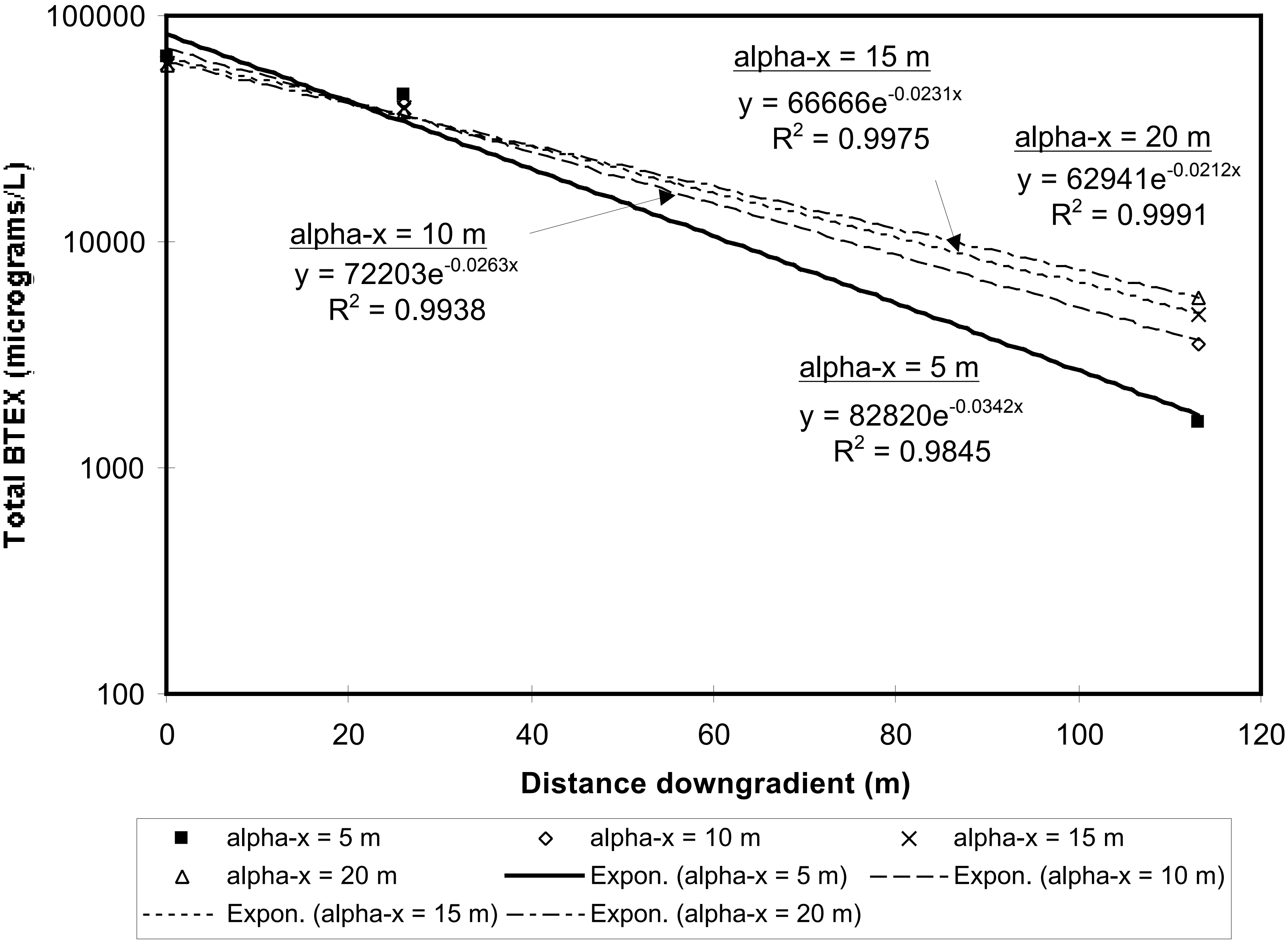

Figure E-3.2. Idealized Domenico (1987) model of concentration versus distance downgradient from source without degradation: Elapsed time = 5000 days, $\alpha_y = 1$ m.

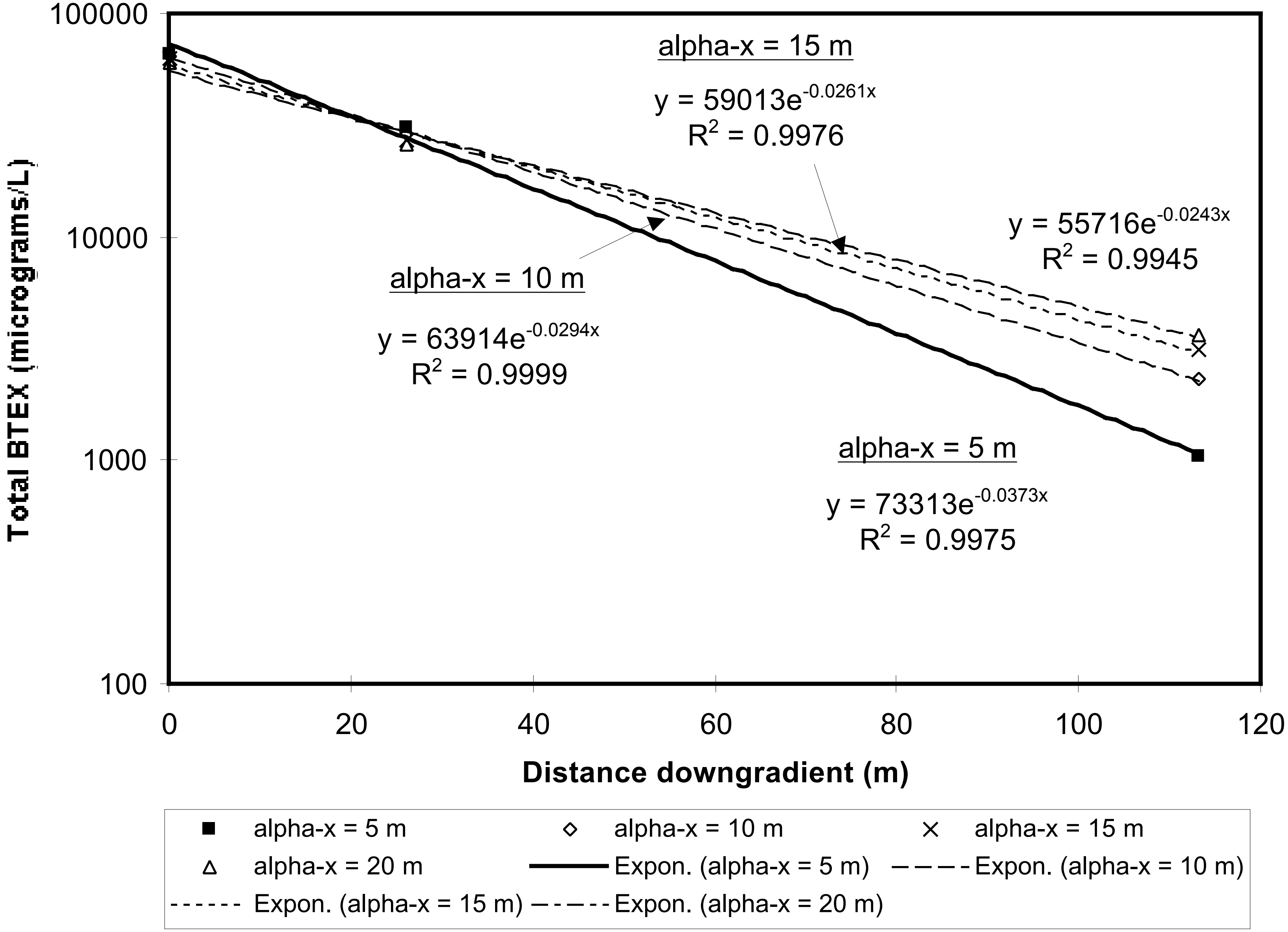

Figure E-3.3. Idealized Domenico (1987) model of concentration versus distance downgradient form source without degradation: Elapsed time = 5000 days, α_y = 2.5 m.

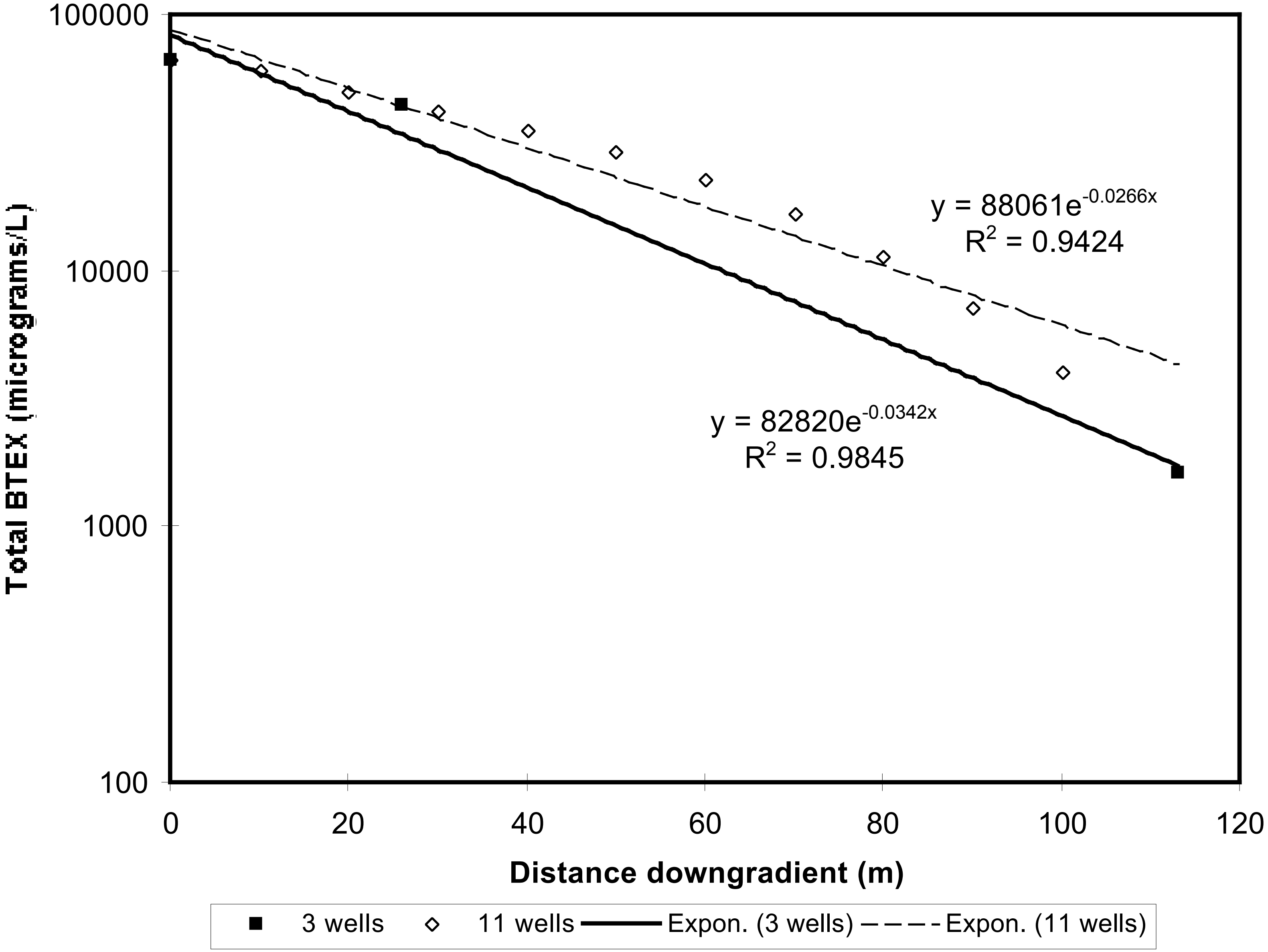

Figure E-3.4. Idealized Domenico (1987) model of concentration versus distance downgradient from source without degradation: Elapsed time = 5000 days, α_x = 5 m, α_y = 1 m.

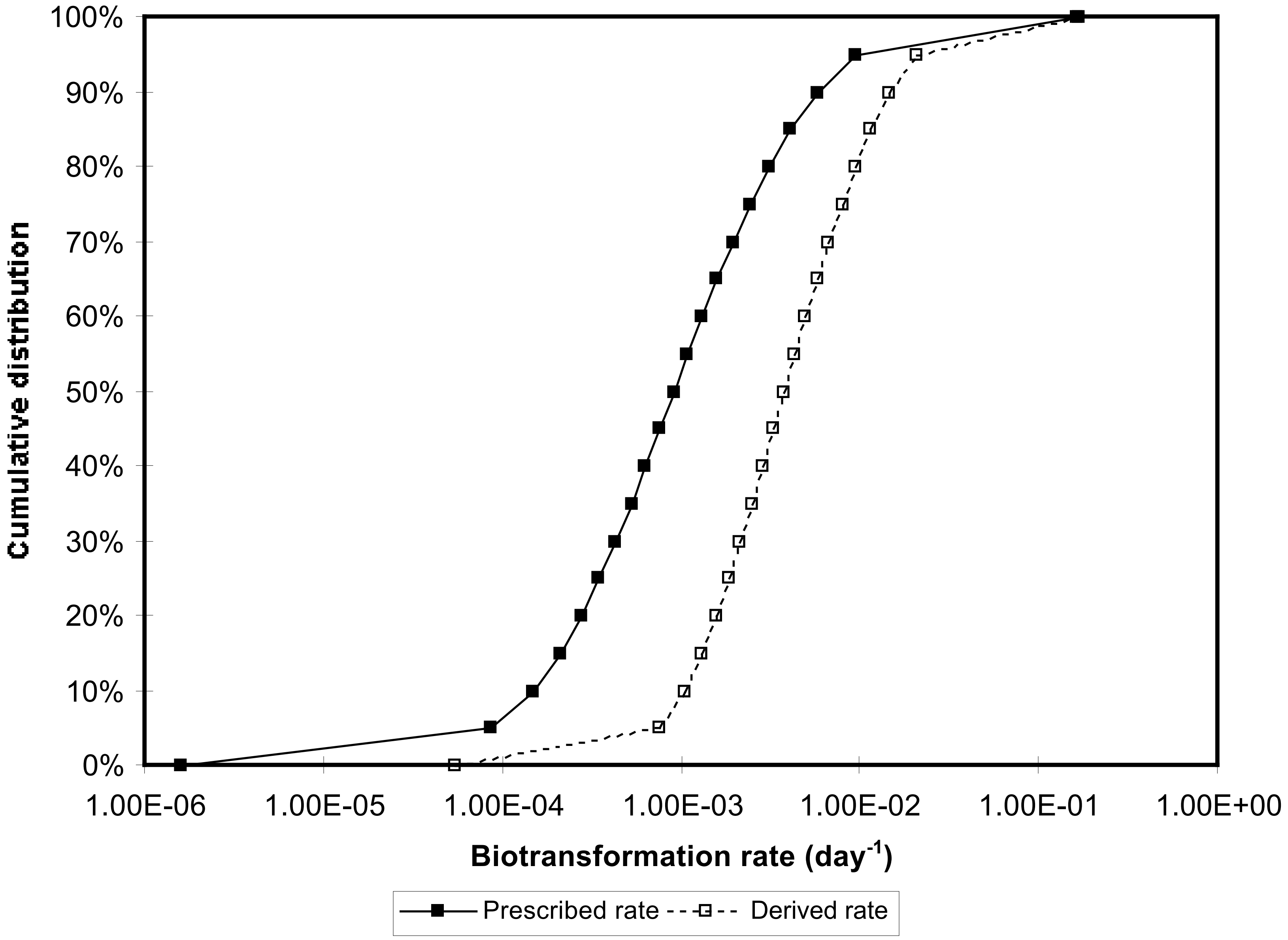

Figure E-3.5. Cumulative distribution of prescribed (input) and derived (output) BTEX biotransformation rates.

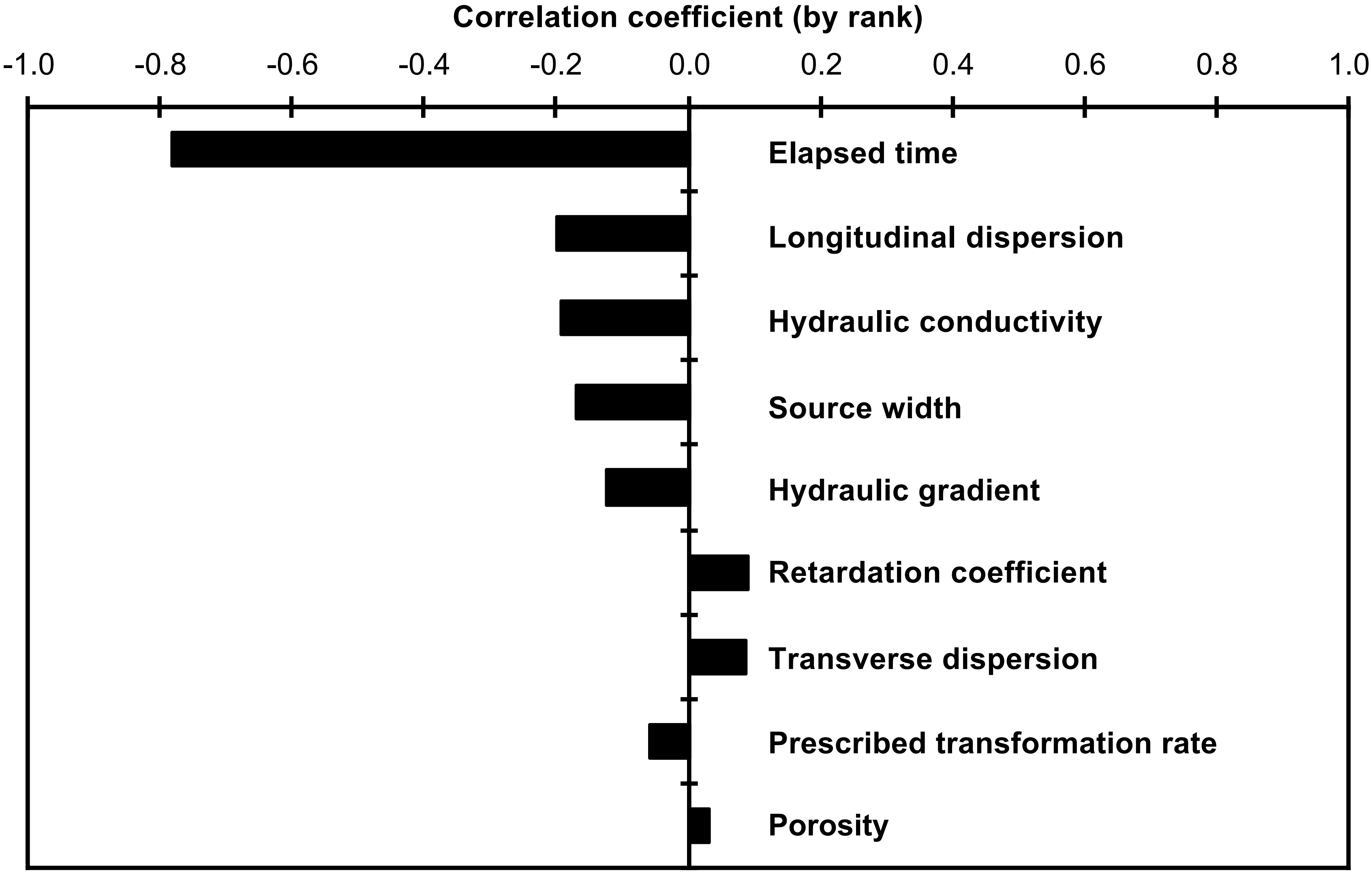

Figure E-3.6. Correlation of estimation error (by rank) with Monte Carlo input parameters.

Appendix E
Section E-4

Estimation of Fuel Hydrocarbon Biodegradation Rates by Integrated Analysis of Plume Lenghts and Bicarbonate Alkalinity

Appendix E (Section E-4)

Estimation of Fuel Hydrocarbon Biodegradation Rates by Integrated Analyses of Plume Lengths and Bicarbonate Alkalinity

E-4.1. Introduction

Dissolved fuel hydrocarbons associated with leaking underground fuel tanks (LUFTs) are known to biodegrade in groundwater under a variety of biogeochemical regimes [Reinhard et al., 1984; Barker et al., 1987; Major et al., 1988; Baedecker et al., 1993; Lovley et al., 1995; Kazumi et al., 1997]. As such, groundwater hydrocarbon plumes may undergo some degree of self-remediation which may limit downgradient migration and hence reduce some of the associated exposure risks [Salanitro, 1993; Rice et al., 1995; Mace et al., 1997]. Even in the presence of a continuous source of fresh contaminants (e.g., from residual free-product lenses in the vadose zone), mass loss through biodegradation, integrated across the spatial extent of the plume, will eventually lead to a steady-state condition in terms of plume length. Clearly, the eventual downgradient extent of such a stable plume, a measure of the risk posed to receptors such as water supply wells, will depend on the overall rate of biodegradation. Moreover, the rate of biodegradation will also strongly influence the amount of time required to effectively remediate a site altogether once the contaminant source is removed. Therefore, a means for estimating mean biodegradation rates at LUFT sites, essentially an inverse problem, is important.

In general, hydrocarbon biodegradation rates are compound-specific and reflect local biogeochemical conditions within a plume (Vroblesky and Chapelle, 1994; Chapelle et al., 1996). Reaction rates have been modeled using Monod-type expressions, accounting for microbiological constraints on substrate utilization (Borden and Bedient, 1986). However, from a practical, field-oriented engineering perspective, a simple first-order kinetic model is often used in site investigations (Wilson et al., 1995; Buscheck et al., 1996). Two techniques are commonly employed to estimate mean first-order biodegradation rates at LUFT sites where the source release history is not well known. One method involves exponential regression of measured concentrations as a function of distance downgradient from the source area along the longitudinal axis of the plume (Buscheck and Alcantar, 1995). This method relies on an expected one-dimensional concentration profile of an ideal plume under steady-state conditions. Although this technique is widely used, the idealized profile is easily influenced by dispersive effects, creating the potential for significant error. A second method involves the normalization of concentrations of degradable hydrocarbon components (e.g., benzene, toluene) by those of presumably recalcitrant constituents, such as tri- and tetramethylbenzene isomers. Changes in the concentration ratios with distance from the source are, in principle, reflective of the rate of biodegradation of the degradable compound of interest. However, the recalcitrance of tri- and tetramethylbenzenes in the multiple biogeochemical zones typically associated with LUFT sites is uncertain (H_ner et al., 1997), so the interpretation of biodegradation rates may be problematic.

The goal of this study is to develop estimates of hydrocarbon biodegradation rates using more direct indicators: limitation of plume length and differences in bicarbonate alkalinity between background and the plume interior (a reflection of hydrocarbon mineralization). The estimates are derived with respect to a population of plumes, rather than for an individual site, and thus are viewed from a probabilistic perspective.

E-4.2. Theory

Several factors will determine the spatial extent of an ideal dissolved hydrocarbon plume emanating from a specified solute flux source. These include mean groundwater velocity, the dispersion coefficients (reflecting the heterogeneous nature of the subsurface), the mean biodegradation rate, the nature of the source term, the retardation coefficient, the porosity, and the aquifer vertical thickness. If mean values were available for a population of LUFT sites and associated hydrocarbon plumes, some degree of inverse correlation would be expected between the mean biodegradation rate and plume length. The scatter in this relationship would reflect the contributions to variance associated with the other variables.

Over a large number of sites, the effects of site-specific features such as pronounced physical heterogeneities in the flow field will tend to average together and thus may be represented conceptually by a simple dispersion model. Thus, macro-scale plume features, such as plume length, may be modeled in a probabilistic sense using Monte Carlo simulation of analytical solutions to the advective-dispersive transport equation. If probability distributions of input variables other than the biodegradation rate are reasonably well-constrained, and if estimates of plume length based on field data from a number of sites can be used for comparison to forecast plume lengths, then a likely range of biodegradation rates which are consistent with observed plumes lengths may be identified.

The effectiveness of using plume length distributions to constrain biodegradation rate distributions by Monte Carlo simulation will depend on two factors. The first is the overall applicability of analytical solutions for probabilistic modeling of groundwater plumes in terms of whether or not all essential features and processes are addressed. The second factor is the choice of probability distribution functions for input parameters (e.g., groundwater velocity, dispersion coefficients) which will obviously exert a major impact on simulation results regardless of the applicability of the analytical solution. To address these issues, a second, independent constraint may be called upon as a consistency check on the simulation results. The eventual end product of hydrocarbon mineralization is CO_2, which combines with water to form carbonic acid, H_2CO_3. In the near-neutral pH environments typically encountered in shallow, alluvial settings where LUFT sites are often found, H_2CO_3 will dissociate into bicarbonate, HCO_3^-, which is often measured in groundwater as bicarbonate alkalinity [*Drever*, 1988]. Indeed, bicarbonate alkalinity has been used a direct indicator of fuel hydrocarbon mineralization in groundwater (**McNab and Dooher, 1998**) **VERIFY YEAR**. Mass-balance constraints implied by reaction stoichiometry, combined with superposition of concentrations given by the analytical solution, permit the calculation of bicarbonate alkalinity values associated with a biodegrading hydrocarbon plume as a function of time and space. Thus, forecast differences in bicarbonate alkalinity between the interior of the plume and background, when compared to the same observations from actual field data, will provide a separate constraint on the range of reasonable biodegradation rates.

E-4.3. Methods

E-4.3.1. Data Collection and Preliminary Screening

Groundwater quality data were available from six LUFT sites located at existing and former military bases in California (Table E-4.1). These include the, the Area 43 Gas Station at Camp Pendleton Marine Corps Base (PMCB), the Petroleum, Oils, and Lubricants Fuel Farm Area at Castle Air Force Base (CAFB) near Merced, the Operable Unit #32 area at George Air Force Base (GAFB) near Victorville, the Building 637 area at the Presidio of San Francisco (PSF), the North-South Gas Station at Travis Air Force Base (TAFB) near Fairfield, and the Base Exchange Service Station at Vandenberg Air Force Base (VAFB) near Lompoc. Data included total petroleum hydrocarbons (TPH) and benzene/toluene/ethylbenzene/xylenes (BTEX), measured by gas chromatography. In addition, geochemical indicator parameters of hydrocarbon biodegradation processes were also measured, typically by ion chromatography or atomic adsorption spectroscopy. These include electron acceptors (dissolved oxygen, nitrate, sulfate) which may be consumed during biodegradation (Borden et al., 1995), ferrous iron and manganese which are mobilized when oxidized forms of these metals in oxyhydroxide minerals are used as electron acceptors (Lovley et al., 1989), and bicarbonate alkalinity and methane as biodegradation products. However, not all of the geochemical indicator data were available from all the sites.

Median values of geochemical parameter values at each of the six sites are shown on Table E-4.2. Interior wells were defined at each site as those wells containing TPH above the applicable detection limit; remaining wells were defined as background wells. Median values, as opposed to mean values, were chosen as representative values from the two categories to minimize the influence of extreme values. Concentration differences in geochemical indicators in plume wells and in background wells can be used to quantitatively compare electron acceptor utilization processes through reaction stoichiometry:

$$C_7H_8 \text{ (toluene)} + 9O_2 + 3H_2O \rightarrow 7HCO_3^- + 7H^+ \qquad \text{(E-4-1)}$$

$$C_7H_8 + 18MnO_2 + 29H^+ \rightarrow 7HCO_3^- + 18Mn^{2+} + 15H_2O \qquad \text{(E-4-2)}$$

$$5C_7H_8 + 36NO_3^- + H^+ \rightarrow 35HCO_3^- + 18N_2 + 3H_2O \qquad \text{(E-4-3)}$$

$$C_7H_8 + 36Fe(OH)_3 + 65H^+ \rightarrow 7HCO_3^- + 36Fe^{2+} + 87H_2O \qquad \text{(E-4-4)}$$

$$2C_7H_8 + 9SO_4^{2-} + 4H^+ + 6H_2O \rightarrow 14HCO_3^- + 9H_2S \qquad \text{(E-4-5)}$$

$$2C_7H_8 + 24H_2O \rightarrow 14HCO_3^- + 9CH_4 + 14H^+ \qquad \text{(E-4-6)}$$

For almost every parameter at every site, differences in median values are consistent with biodegradation. Among the six sites as a whole, sulfate reduction appears to be the dominant process. If the magnitude of a geochemical indicator signature is defined as,

$$\Delta c = c^{*}_{plume} - c^{*}_{bkg} \tag{E-4-7}$$

where c^{*}_{plume} and c^{*}_{bkg} refer to the respective median plume interior and median background concentrations, then an inverse relationship should exist between Δc defined with respect to bicarbonate alkalinity (an expected positive value) and Δc defined with respect sulfate (an expected negative value). The relationship between *Δc-bicarbonate alkalinity* and *Δc-sulfate* for the six sites, based on Table E-4.2, is shown on Figure E-4.1, along with the ideal Δc relationship if sulfate reduction (Eq. E-4-5) were the only process affecting *Δc-bicarbonate alkalinity*. Given the approximate nature of the definition of Δc in Eq. E-4-7, the relationship between bicarbonate alkalinity and sulfate Δc values is compelling; the offset of the field estimates from the ideal relationship likely reflects the roles of other electron acceptors in influencing changes in bicarbonate alkalinity across the plumes. The internal consistency between bicarbonate alkalinity and sulfate geochemical indicators provides supporting evidence that bicarbonate alkalinity may be used to constrain the progress of biodegradation.

Plume lengths at the six sites were defined as the approximate distance from the source area to the downgradient edge of the TPH plume at the 10 parts-per-billion (ppb) contour level. Estimated plume lengths, based on two-dimensional TPH contour maps for each site, are shown on Table E-4.3.

E-4.3.2. Modeling Approach

Wilson and Miller (1978) presented an analytical solution for solute transport in a homogeneous, infinite aquifer of constant thickness with a uniform fluid flow field, assuming an instantaneous point source. When integrated over time, the source term is transformed into one of continuous mass injection,

$$c(x,y,t) = \int_{\tau=0}^{\tau=t} \frac{M_f}{4\pi\phi\tau H\sqrt{D_l D_t}} \exp\left[-\frac{(x-v\tau)^2}{4D_l\tau} - \frac{y^2}{4D_t\tau} - \lambda\tau\right] d\tau \tag{E-4-8}$$

where M_f is the mass introduced per unit time, ϕ the porosity, H the aquifer thickness, D_l and D_t the respective longitudinal and transverse dispersion coefficients, v the ground water velocity, λ the first-order decay coefficient, x and y, the spatial coordinates relative to the source location, and t the elapsed time between source introduction and sampling time. Given a set of values for the governing parameters in Eq. E-4-8, TPH concentrations may be predicted as a function of space and time. Plume length may be quantified along the longitudinal plume axis by setting $y = 0$ and solving for x, where c equals some prescribed concentration, using a search algorithm (e.g., bisection, Newton's method).

At (x,y), the cumulative quantity of dissolved hydrocarbons which have undergone biodegradation, Δd, is given by superposition according to,

$$\Delta d(x,y,t) = \int_{\tau=0}^{\tau=t} \frac{M_f}{4\pi\phi\tau H\sqrt{D_l D_t}} \exp\left[-\frac{(x-v\tau)^2}{4D_l\tau} - \frac{y^2}{4D_t\tau}\right] d\tau - \int_{\tau=0}^{\tau=t} \frac{M_f}{4\pi\phi\tau H\sqrt{D_l D_t}} \exp\left[-\frac{(x-v\tau)^2}{4D_l\tau} - \frac{y^2}{4D_t\tau} - \lambda\tau\right] d\tau \tag{E-4-9}$$

The generation of excess bicarbonate alkalinity over background may be estimated at any (x,y) by assuming a surrogate hydrocarbon compound such as toluene, C_7H_8, represents the soluble, potentially biodegradable fraction of hydrocarbon which is measured as TPH at a given site. A value for Δ*c-bicarbonate alkalinity* may then be defined in a manner analogous to the field data definition (Eq. E-4-6) by populating the spatial domain associated with each plume with a random distribution of monitoring wells.

At any given site, the representative values of the parameters in Eq. E-4-8 and Eq. E-4-9 that produce the most accurate model of the hydrocarbon plume and bicarbonate alkalinity plumes are generally unknown. However, field data and practical judgment may be used to place constraints on these values in the form of probability distribution functions. These probability distributions may be then be used in Monte Carlo simulations to generate multiple data sets representing a large number of idealized plumes. Specific simulation output consists of a set of plume lengths and associated Δ*c-bicarbonate alkalinity* values characteristic of the synthetic plume population.

Probability distribution functions for the governing parameters in Eq. E-4-8 and Eq. E-4-9 are listed on Table E-4.4. A total of 500 Monte Carlo realizations were generated from these distributions using the Crystal Ball add-in package for Microsoft Excel (Decisioneering, Inc., 1996). A stand-alone computer program was written to calculate plume lengths and Δ*c-bicarbonate alkalinity* values (using five to fifteen fictitious monitoring wells placed at random locations in the vicinity of each plume).

E-4.4. Results and Discussion

Rank-based correlation coefficients illustrating the relationships between model output (plume length and Δ*c-bicarbonate alkalinity*) and input parameters are given on Table E-4.4. Among the input parameters and the associated probability distributions, variance in groundwater velocity and the biodegradation rate appear to largely control the variance in either model output. In retrospect, therefore, the choices of probability distributions for the other parameters (source term, aquifer thickness, dispersivity, age of plume) do not seem to be especially critical for the purposes of these simulations.

Inverse correlation characterizes the relationship between Δ*c-bicarbonate alkalinity* and plume length (defined by the 10 ppb contour) among the synthetic plume population (Figure E-4.2). Intuitively, this is expected since low biodegradation rates tend to produce longer plumes and low Δ*c-bicarbonate alkalinity* values, whereas the opposite is expected for high biodegradation rates (the extreme values present at either end of the graph reflect unrealistic biodegradation rates, coupled with particular chance combinations of the other variables). The relationship between these two plume metrics for the six field sites are also shown. The field observations are in generally good agreement with the synthetic plume metrics. The notable exception is the plume associated with the PMCB site, which appears to be too short given the observed Δ*c-bicarbonate* *alkalinity* value. However, this plume is truncated by discharge into a creek approximately 30 m downgradient from the source area. In the absence of the creek, the plume would be expected to extend further and thus would plot more toward the centerline shown on Figure E-4.2.

The forecast relationship between the biodegradation rate, λ, and Δ*c-bicarbonate alkalinity* is shown on Figure E-4.3. An overall positive trend is apparent in the forecasts, although a great deal of scatter exists in the relationship (Table E-4.4). Assuming a lognormal distribution of Δ*c-bicarbonate alkalinity* among the field data collected from the six sites, the values bracketed by one standard deviation range from 67 mg/L to 215 mg/L. The corresponding range of λ-values (bracketed by one standard deviation) falls between 4×10^{-4} and 7×10^{-3} day^{-1}, with a geometric mean of 1.6×10^{-3} day^{-1}. According to the model, lambda values above or below this interval would generally produce plumes with Δ*c-bicarbonate alkalinity* values that would fall outside of those commonly observed in the field.

By itself, this constraint on lambda-values is tenuous because of the many simplifying assumptions in the model and the definition of Δ*c-bicarbonate alkalinity* itself. However, plume length serves as an additional model output metric that can be used as an independent check on λ. The modeled relationship between λ and plume length is shown on Figure E-4.4. An overall negative trend is apparent in the forecasts, again with considerable scatter. Assuming a lognormal distribution of plume lengths for TPH among the six sites, the values bracketed by one standard deviation range from 56 m to 394 m. The corresponding range of λ-values (bracketed by one standard deviation) falls between 4×10^{-4} and 9×10^{-3} day^{-1}, with a geometric mean value of 1.9×10^{-3} day^{-1}.

Considering the broad simplifying assumptions inherent in the modeling, and the uncertainties in model parameters, the near-perfect agreement for the range of λ-values may well involve an element of chance. Nevertheless, the model does constrain the likely range of degradation rates to be on the order of 3×10^{-4} to 9×10^{-3} day^{-1} for the selected sites. Values of λ outside of this range would be expected to yield Δ*c-bicarbonate alkalinities* and plume lengths that are not consistent with observation. Moreover, this range of values is consistent with first-order reaction rates estimated in other field studies. A review of published degradation rates estimated from field data under a variety of biogeochemical regimes (Table E-4.5) indicates a geometric mean value of 3×10^{-3} day^{-1}, with a range encompassed by one standard deviation (lognormal distribution) of 4×10^{-4} to 3×10^{-2} day^{-1} (Figure E-4.5).

The mean biodegradation rates estimated by this study hold significant implications for remedial decision making. If rates of this order are supplied to Eq. E-4-8, along with median values from the probability distributions given on Table E-4.4, the analytical model predicts that such a plume would stabilize after only 10 to 15 years, no longer posing a threat to potential downgradient receptors. This prediction is actually conservative, given that the model assumes a source that is continuously active. When source removal activities occur, such as LUFT excavation and removal, such plumes would begin to decrease in size. These results may explain the recent empirical studies of Rice et al., 1995 and Mace et al., 1997, which indicated that the majority of existing LUFT-associated hydrocarbon plumes appear to be stable or declining under natural conditions, whereas only a small fraction appear to be experiencing further growth.

E-4.5. 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 ground water," *Applied Geochemistry*, **8**(6) 569–586.

Barker, J. F., G. C. Patrick, and D. Major (1987), "Natural attenuation of aromatic hydrocarbons in a shallow sand aquifer," *Ground Water Monitoring and Remediation*, Winter, 64–71.

Borden, R. C., and P. B. Bedient (1986), "Transport of dissolved hydrocarbons influenced by oxygen-limited biodegradation **1**, Theoretical development, Water Resources Research, **22**(13), 1973–1982.

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

Borden, R. C., R. A. Daniel, L. E. LeBrun, C. W. Davis (1997), "Intrinsic biodegradation of MTBE and BTEX in a gasoline-contaminated aquifer," *Water Resources Research*, **33**(5), 1105–1115.

Buscheck, T. E., and C. M. Alcantar (1995), "Regressive techniques and analytical solutions to demonstrate intrinsic bioremediation," in *Intrinsic Bioremediation,* R. E. Hinchee, J. T. Wilson, and D. Downey, Eds. (Battelle Press, Columbus, Ohio) pp. 109–116.

Buscheck, 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. Vroblesky (1996), "Measuring rates of biodegradation in a contaminated aquifer using field and laboratory methods," *Ground Water* **34**(4), 691–698.

Cozzarelli, I. M., R. P. Eganhouse, and M. J. Baedecker (1990), "Transformation of monoaromatic hydrocarbons to organic acids in anoxic groundwater environment," *Environmental Geology and Water Science*, **16**(2), 135–141.

Decisioneering, Inc. (1996), Crystal Ball: Forecasting and Risk Analysis for Spreadsheet Users. Decisioneering, Inc., Aurora, Colorado.

Drever, J. I., (1988), "The Geochemistry of Natural Waters" (Prentice-Hall, Englewood Cliffs, New Jersey), 437 p.

H_ner, A., P. H_hener, and J. Zeyer (1997), "Degradation of trimethylbenzene isomers by an enrichment culture under N_2O-reducing conditions," *Applied and Environmental Microbiology*, **63**(3), 1171–1174.

Kazumi, J., M. E. Caldwell, J. M. Suflita, D. R. Lovley, and L. Y. Young (1997), "Anaerobic degradation of benzene in diverse anoxic environments," *Environmental Science and Technology*, **31**(3), 813–818.

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**(3), 953–958.

Mace, R. E., R. S. Fisher, D. M. Welch, and S. P. Parra (1997), "Extent, Mass, and Duration of Hydrocarbon Petroleum Storage Tank Sites in Texas," *Bureau of Economic Geology*, University of Texas at Austin.

Major, D. W., C. I. Mayfield, and J. F. Barker (1988), "Biotransformation of benzene by denitrification in aquifer sand," *Ground Water* , **26**(1), 8–14.

McNab, W. W., Jr., and B. P. Dooher (1998), "Uncertainty analyses of fuel hydrocarbon biodegradation signatures in ground water by probabilistic modeling," *Ground Water*, **36**(4), 691–698.

Reinhard, M., N. L. Goodman, and J. F. Barker (1984), "Occurrence and distribution of organic chemicals in two landfill leachate plumes," *Environmental Science and Technology*, **18**(12), 953–961.

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).

Rifai, H. S., R. C. Borden, J. T. Wilson, and C. H. Ward (1995), "Intrinsic bioattenuation for subsurface restoration," in *Intrinsic Bioremediation,* Hinchee, R. E., J. T. Wilson, and D. C. Downey, Eds. (Battelle Press, Columbus, Ohio), pp. 1–29.

Salanitro, J. P. (1993), "The role of bioattenuation in the management of aromatic hydrocarbon plumes in aquifers," *Ground Water Monitoring and Remediation*, Fall, 150–161.

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.

Wiedemeier, T. H., et al. (1995), "Patterns of intrinsic bioremediation at two US Air Force Bases," in *Batelle Institute Proceedings of the Third Bioremediation Conference*, Hinchee, R. E., J. T. Wilson, and D. C. Downey, Eds., **3**(1), 32–51.

Wiedemeier, T. H., M. A. Swanson, J. T. Wilson, D. H. Kampbell and others (1996), "Approximation of biodegradation rate constants for monoaromatic hydrocarbons (BTEX) in ground water," *Ground Water Monitoring and Remediation*, Summer, **16**(3), 186–194.

Wilson, B. H., J. T. Wilson, D. H. Kampbell, B. E. Bledsoe, and J. M. Armstrong (1990), "Biotransformation of monoaromatic and chlorinated hydrocarbons at an aviation gasoline spill site," *Geomicrobiology*, **8**(3/4), 225–40.

Wilson, B. H., J. T. Wilson, and D. Luce (1996), "Design and interpretation of microcosm studies for chlorinated compounds," in *Symposium on Natural Attenuation of Chlorinated Organics in Ground Water*, Dallas, Texas, September 11–13 (EPA/540/R-96/509), pp. 21–28.

Wilson, J. L., and P. G. Miller (1978), "Two-dimensional plume in uniform ground-water flow," Journal of the Hydraulics Division, in *Proceedings of the American Society of Civil Engineers*, **104**(4), pp. 503–514.

Wilson, J. T., D. H. Kampbell, and J. Armstrong (1994), "Natural bioreclamation of alkylbenzenes (BTEX) from a gasoline spill in methanogenic groundwater," in *Hydrocarbon Bioremediation*, Hinchee, R. E., B. C. Alleman, R. E. Hoeppel, and R. N. Miller, Eds. (Lewis Publishers, Boca Raton, Florida), pp. 201–218.

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*, Hinchee, R. E., J. T. Wilson, and D. C. Downey, Eds. (Battelle Press, Richland, Washington), pp. 91–100.

Table E-4.1. Sites included in study.

LUFT site location	Hydrogeologic setting	Contaminant	Number of monitoring wells	Analytes
Camp Pendleton Marine Corps Base (PMCB)	Coastal canyon alluvium and fill	Gasoline	16	TPH, BTEX, HCO3- (as alkalinity), CH4, Eh, Fe2+, O2, NO3-, pH, SO42
Castle Air Force Base (CAFB)	Broad alluvial plain	Aviation fuel (JP-4)	19	TPH, BTEX, HCO3- (as alkalinity), CH4, Eh, Fe2+, Mn2+, O2, NO3-, pH, SO42
George Air Force Base (GAFB)	High desert alluvial fan	Aviation fuel (JP-4)	16	TPH, BTEX, HCO3- (as alkalinity), CH4, Eh, Fe2+, Mn2+, O2, NO3-, pH, SO42
Presidio of San Francisco (PSF)	Shallow marine deposits, organic-rich	Gasoline and diesel	13	TPH, BTEX, HCO3- (as alkalinity), CH4, Eh, Fe2+, Mn2+, O2, NO3-, pH, SO42
Travis Air Force Base (TAFB)	Broad alluvial plain	Gasoline	29	TPH, BTEX, HCO3- (as alkalinity), CH4, Eh, Fe2+, Mn2+, O2, NO3-, pH, SO42
Vandenberg Air Force Base (VAFB)	Shallow marine deposits	Gasoline	14	TPH, BTEX, HCO3- (as alkalinity), CH4, Eh, Fe2+, Mn2+, NO3-, pH, SO42

Table E-4.2. LUFT site geochemical indicator data (concentrations given in mg/L).

Species	Zone	PMCB	CAFB	GAFB	PSF	TAFB	VAFB
O_2	Plume	0.65	2.1	3.4	0.4	0.2	[*]n.a.
	Background	1	2.9	6.4	0.3	0.5	n.a.
	Δc	-0.35	-0.8	-3.0	0.1	-0.3	n.a.
NO_3^-	Plume	1.6	2.8	0.3	0.01	0.3	0.05
	Background	3.2	6.5	1.4	0.06	5.5	0.07
	Δc	-1.6	-3.7	-1.1	-0.05	-5.2	-0.02
SO_4^{2-}	Plume	70.4	15.9	53	10.2	456	3.9
	Background	84	27.1	137.5	48.3	740	200
	Δc	-13.6	-11.2	-84.5	-38.1	-284	-196.1
Fe^{2+}	Plume	1.5	0.05	0.05	4.7	2.97	3.3
	Background	0	0.007	0	0.03	0.02	0.8
	Δc	1.5	0.043	0.05	4.67	2.95	2.5
Mn^{2+}	Plume	n.a.	0.88	1.5	0.78	2.9	0.50
	Background	n.a.	0.5	0	0.43	0.2	0.22
	Δc	n.a.	0.38	1.5	0.35	2.7	0.28
[†]HCO_3^-	Plume	466	262	252	500	621	500
	Background	393	182	176	383	327	300
	Δc	73	80	76	117	294	200
CH_4	Plume	0.9	0.006	0.002	7	0.21	0.26
	Background	0.006	0.0006	0.0002	0.3	0.005	0.004
	Δc	0.9	0.0054	0.0018	6.7	0.205	0.256

Table E-4.3. Inferred TPH plume lengths, as defined by the 10 part-per-billion contour line.

Site	Plume length (m)
PMCB	30
CAFB	210
GAFB	610
PSF	180
TAFB	120
VAFB	120

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[*] n.a. = data not available.

[†] Reported as bicarbonate alkalinity.

Table E-4.4. Probability distributions used in Monte Carlo realizations.

Parameter	Probability distribution[1]	Basis	R (Plume length)	R(calk)
Source term (Mf)	18,900 - 151,400 liters	Postulated.	0.08	0.09
Aquifer thickness (H)[2]	4.6 1.5 m	Site hydrostratigraphies.	-0.04	-0.13
Groundwater velocity (v)	0.003 - 1.0 m/day	Estimated mean hydraulic conductivities by pumping tests; interpolated mean hydraulic gradient, Darcy's law.	0.68	-0.69
Degradation coefficient ()	0.01% - 2% day-1	Postulated based on commonly reported range in the literature.	-0.57	0.35
L:L ratio[3]	0.03 - 0.33	Assumed dispersivity to plume length scale ratio.	0.13	-0.02
T:L ratio	0.003 - 0.03	Assumed dispersivity to plume length scale ratio.	-0.03	-0.11
Elaped time since source initiation (t)[4]	20 - 40 years	Site histories.	0.09	-0.12

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[1] As defined by the applicable analytical detection limit, typically equal to or less than 1 μg/L.

[2] Includes wells sampled as part of site natural attenuation assessment; does not include all monitoring wells at each site.

[3] Considered only when detected in five or more wells.

[4] Best-fit between normal and lognormal distributions determined by the Kolmogorov-Smirnov test.

Table E-4.5. Selected published reaction rates for benzene estimated from field data at groundwater contamination sites.

Conditions	Rate (day^{-1})	Reference
Iron-reducing	1.1×10^{-4}	*Wilson et al.* (1996)
Iron-reducing	2.0×10^{-4}	*Rifai et al.* (1995)
Nitrate-reducing, sulfate-reducing, and methanogenic	4.3×10^{-4}	*Wilson et al.* (1994)
Nitrate-reducing	9.0×10^{-4}	*Borden et al.* (1997)
Iron-reducing	2.2×10^{-3}	*Wilson et al.* (1996)
Methanogenic	7.1×10^{-3}	*Wilson et al.* (1990)
Sulfate-reducing	1.8×10^{-2}	*Wiedemeier et al.* (1995)
Methanogenic	1×10^{-2}	*Wiedemeier et al.* (1995)
Methanogenic, iron-reducing, manganese-reducing	1.7×10^{-2}	*Cozzarelli et al.* (1990)
Sulfate-reducing	2.8×10^{-2}	*Wiedemeier et al.* (1996)
Sulfate-reducing	3.8×10^{-2}	*Wiedemeier et al.* (1996)

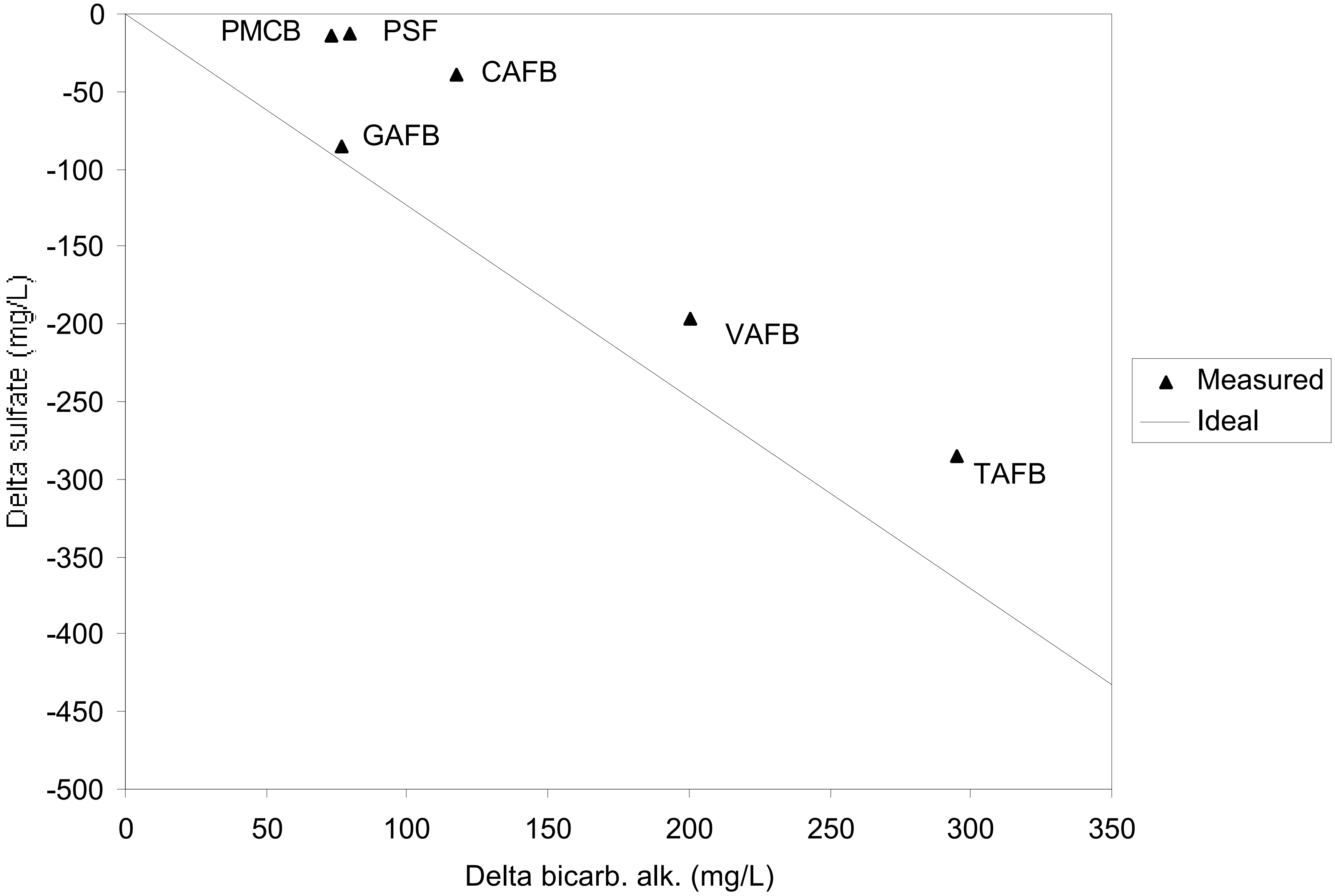

Figure E-4.1. Relationship between Δ*c-sulfate* and Δ*c-bicarbonate alkalinity*.

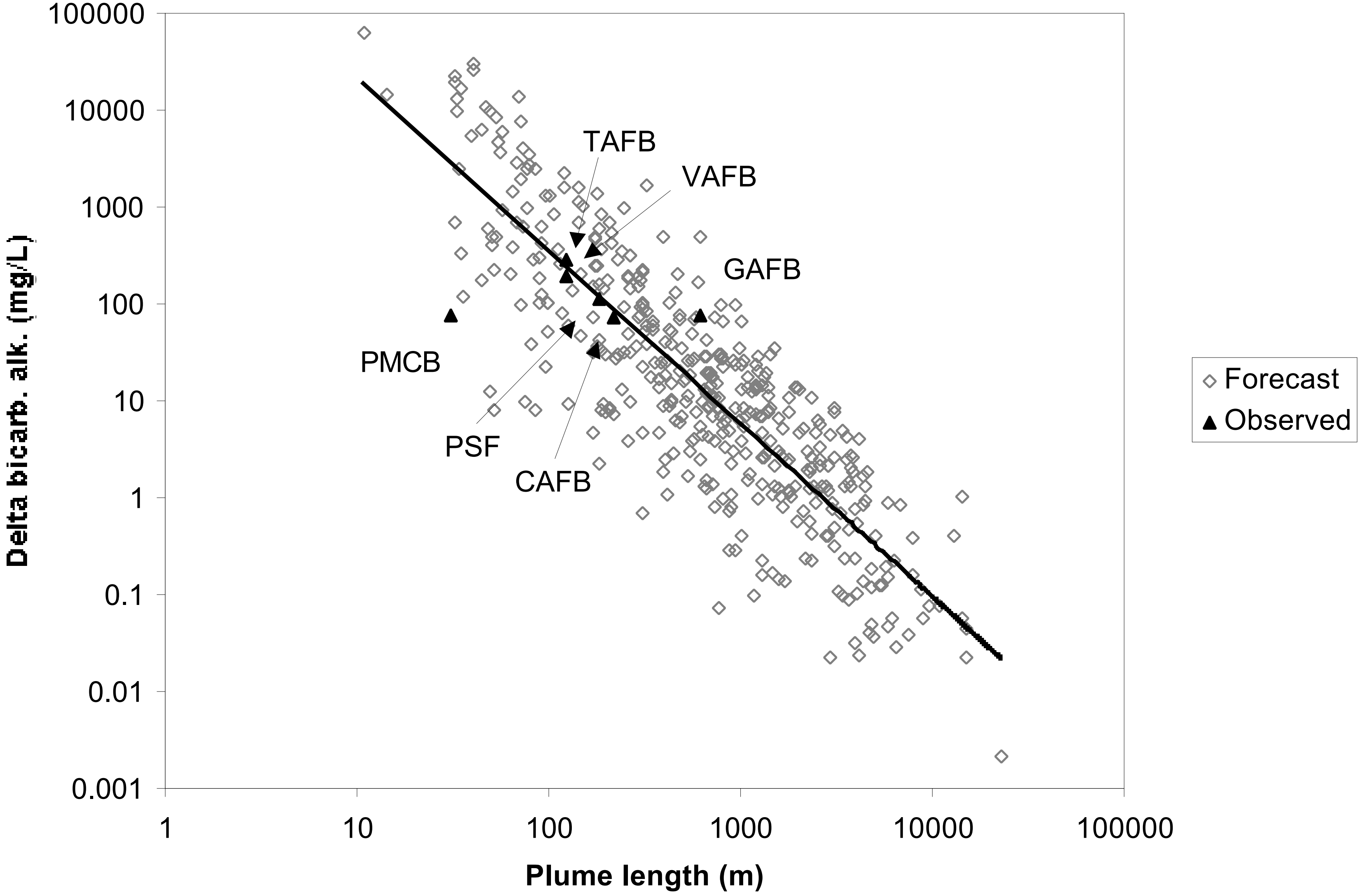

Figure E-4.2. Relationship between plume length and Δ*c-bicarbonate alkalinity* for Monte Carlo realizations (forecast synthetic plumes) and field data.

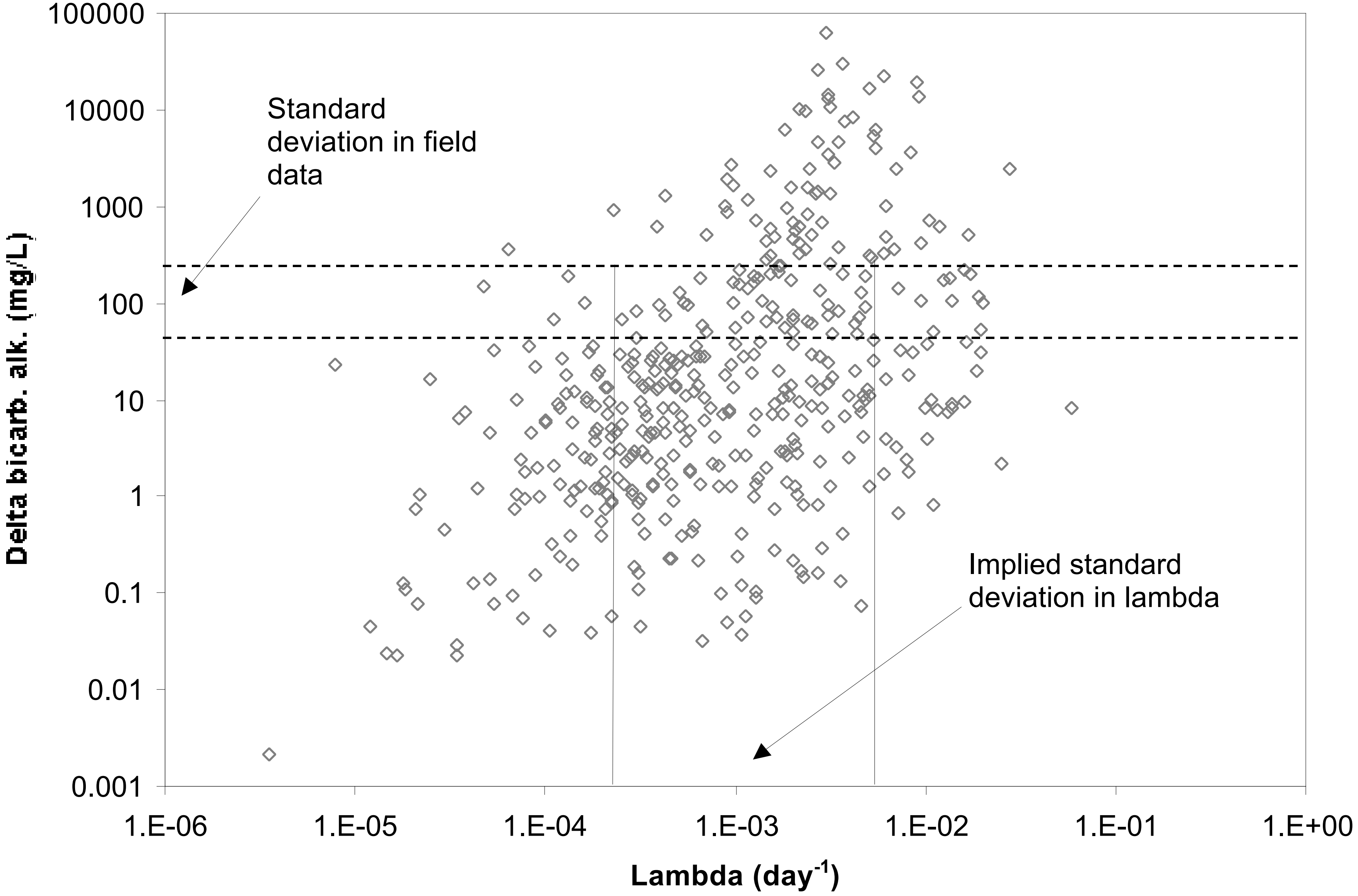

Figure E-4.3. Relationship between Δ *c-bicarbonate alkalinity* and degradation rate (λ) in forecast synthetic plumes.

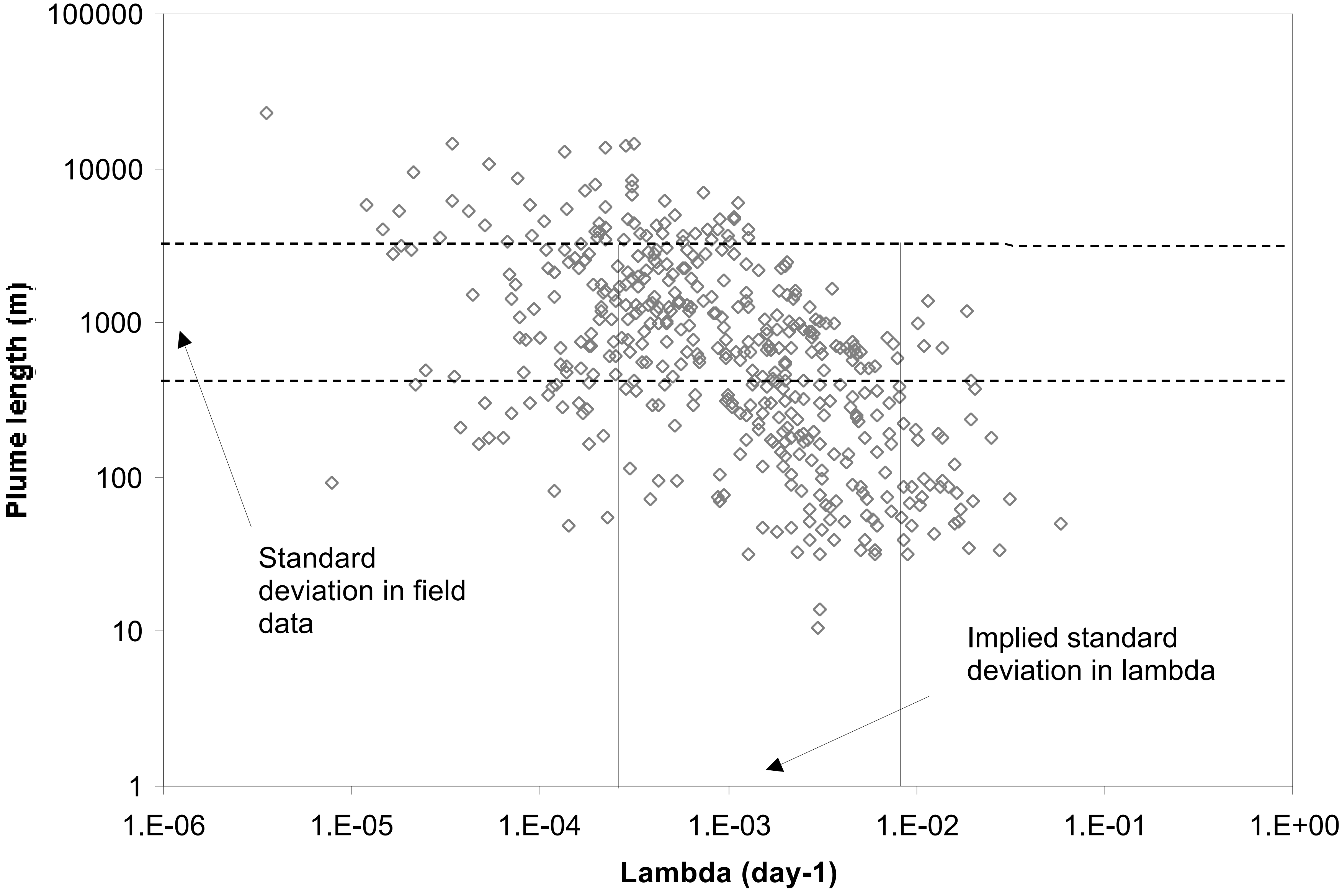

Figure E-4.4. Relationship between plume length and degradation rate (λ) in forecast synthetic plumes.

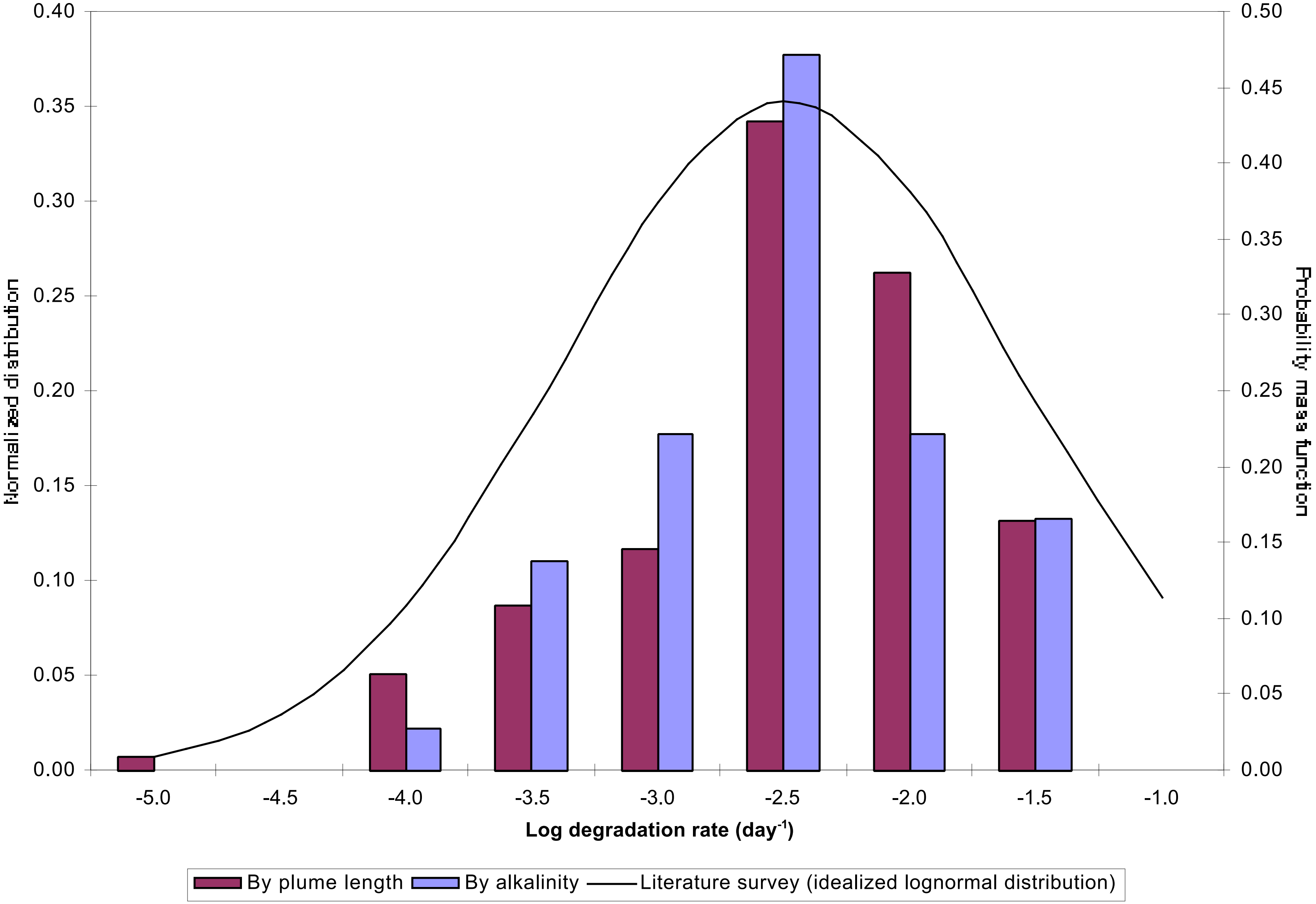

Figure E-4.5. Probability distributions of degradation rates; literature (for benzene) and this study (for TPH as gasoline).

Appendix F

Summary of Recent MTBE Information

Appendix F

Summary of Recent MTBE Information

Michael C. Kavanaugh

Methyl *tertiary* butyl ether (MTBE) was first added to gasoline as an octane enhancer in 1979, but did not become widely used in California until approximately 1986. California is one of fifteen states in the U.S. currently required to use reformulated gasoline which contains MTBE in order to meet the 1990 amendments to the Clean Air Act. Reformulated gasoline in California may contain oxygenates such as MTBE at concentrations up to 11 percent by volume in order to meet the gasoline oxygen content requirements specified by the Clean Air Act and the California Air Resources Control Board. Although other oxygenates such as ethanol can meet the oxygen requirements for reformulated gasoline, MTBE has become the oxygenate of choice for a number of technical and economic reasons. As MTBE use has spread, the incidence of finding MTBE at sites that have experienced releases of fuel hydrocarbons has increased dramatically. Recent surveys have shown that MTBE is present in the groundwater at over 90 percent of the leaking underground storage tank (UST) sites.

Currently, MTBE is not a regulated chemical in drinking water at the Federal or State levels, but due to recent legislation, California's Department of Health Services (DHS) have established a proposed secondary maximum contaminant level (SMCL) of 5 ppb. A primary MCL will be proposed by July 1999. The human toxicity of MTBE via ingestion is also uncertain, and EPA currently considers MTBE to be a possible human carcinogen. CALEPA's Office of Environmental Health Hazard Assessment (OEHHA) has proposed a public health goal (PHG) of 14 ppb for MTBE (OEHHA, 1998). DHS will utilize the PHG in the development of the primary MCL for MTBE. With respect to acute aquatic toxicity, MTBE appears to be significantly less toxic to organisms tested compared to benzene, for example. The current action level for MTBE in California is 35 µg/L, but the SMCL is lower than this value due to taste and odor effects, which may be perceptible to some portions of the population at levels as low as 5 µg/L. Because of this concern, EPA recently lowered its range of advisory levels for MTBE from 20 to 200, to 20 to 40 µg/L. Thus, recommended cleanup levels for this compound are likely to be between 5 and 20 µg/L, if the ground water is a potential source of drinking water as defined by California State Water Code.

Whether or not MTBE and other ether oxygenates, such as tertiary amyl methyl ether (TAME), or ethyl *tertiary* butyl ether (ETBE) will degrade in ground water via abiotic or biotic mechanisms is a current focus of considerable research. Early investigations provided ambiguous and conflicting results (references), which indicated that degradation, if it was occurring it was exclusively by means of biotic mechanisms. These early studies indicated that MTBE did not degrade under anaerobic conditions, but that under aerobic conditions, biodegradation may occur. Studies of abiotic degradation have thus far shown that MTBE will not degrade chemically, unless a highly oxidizing environment can be simulated, such as occurs in an ex-situ advanced oxidation process. Such conditions will not occur naturally in the subsurface.

More recent studies (Salanitro, 1994; Park & Cowan, 1997) have isolated microorganisms that can degrade MTBE in laboratory microcosms, provided that the oxygen content exceeds 2 mg/L. Recent field studies also report promising indications that MTBE will degrade aerobically in the subsurface, provided that sufficient oxygen is present (Javanumardian, 1997; Carter, 1997; Regenesis, 1998). A variety of studies have also shown, however, that in the presence of BETX, and other relatively easily degradable organic compounds, MTBE degradation does not occur, presumably because of competitive inhibition between MTBE and the aromatic compounds. Shortage of oxygen may also explain these observed results, due to the presence of high concentrations of degradable compounds that cause rapid exhaustion of the oxygen in the water.

The microbial kinetics of MTBE degradation are still under investigation, but results should be available soon that will permit estimates of MTBE degradation under a variety of geochemical conditions. It is likely, as has been reported by at least one investigator (Borden, 1997), that under optimum conditions in the subsurface, MTBE will degrade at a rate at least one order of magnitude less rapidly than benzene. All microcosm studies have also indicated that for microorganisms capable of degrading MTBE, there is a significant lag phase that may extend up to one year, before the microbial population is capable of degrading MTBE. Under conditions of rapid ground water movement, greater than 1 meter per day, this lag phase may result in very long MTBE plumes, which is the situation observed at Port Hueneme. Benzene degradation rates reportedly range from less than 0.1 percent per day up to more than 1 percent per day, depending on the geochemical conditions. The average rate of benzene degradation observed in the LUFT study by LLNL was 0.8 percent per day, which translates into a half life of about 86 days. Thus, the most recent data on MTBE biodegradation in ground water suggest that if MTBE does degrade biotically, it likely will occur at the edges of the plume, and only when the MTBE migrates beyond the boundary of the BETX plumes. Because of the apparent slow rate of growth of microbial populations capable of degrading MTBE, and the apparent long lag phase of microbial growth, the potential for long MTBE plumes that may adversely impact large volumes of ground water is high.

Reference

Borden, R., R. Daniel, L. LeBrun IV, and C. Davis (1997), "Intrinsic biodegradation of MTBE and BTEX in a gasoline-contaminated aquifer," *Water Resources Research*, **33**(5), 1150–1115, P:\31\95\001\reports\citation.doc.

Carter, S. R., J. M. Bullock, and W. R. Morse (1997), "Enhanced Biodegradation of MTBE and BTEX Using Pure Oxygen Injection," abstract in papers from the *Fourth International In Situ and On-Site Biodegradation Symposium*, vol. 4, April 28 ñ May 1, 147 pp.

Javanumardian, M., and H. A. Glasser (1997), "In-Situ Biodegradation of MTBE Using Biosparging," in *Proceedings of the American Chemical Society*, vol. 37, San Francisco, Calif., April 13–17.

Office of Environmental Health Hazard Assessment (OEHHA) (1998), *Public Health Goal for Methyl Tertiary Butyl Ether (MTBE in Drinking Water* (Draft).

Park, K., and R. M. Cowan, (1997), "Effects of oxygen and temperature on the biodegradation of MTBE," in *Proceedings of the 213th ACS National Meeting*, Preprints of Extended Abstracts **37**(1), 421–423, San Francisco, Calif.

Regenesis (1998), “Potential for Biodegradation of Methyl Tertiary Butyl Ether (MTBE),” *ORC Technical Bulletin #5-6.0*, Regenesis Bioremediation Products, San Juan Capistrano, Calif., 5 pp.

Salanitro, J. P., L. A. Diaz, M. P. Williams, and H. L. Wisniewski (1994), “Isolation of a bacterial culture that degrades methyl t-butyl ether,” *Applied and Environmental Microbiology*, **60**(7), 2593–2596.

Appendix G

Cone Penetrometry

Appendix G

Cone Penetrometry

The real-time availability of information is critical and part of an observational approach to site characterization where a conceptual model of the site is continually re-evaluated as data is iteratively gathered and interpreted . The refined conceptual model guides the placement of the next sampling location. The cone penetrometer system is especially attractive when the cost of quarterly monitoring ground water wells is considered in assessing the cost of site characterization. The results of a cone penetrometer survey can be used to identify the optimum location for final soil borings and ground water monitoring wells for the purpose of long-term monitoring and remediation.

The typical cone penetrometer is mounted on a 20- to 60-ton truck and driven to the site requiring characterization. Cone penetrometer tools can collect both soil and groundwater samples as well as soil gas samples. A conical rod is hydraulically pushed into the ground. Some rigs are equipped with a hammer assist. The push rod tip can be equipped with a variety of sensors or soils and groundwater sampling tools. The cone penetrometer can characterize several important leaking underground fuel tank (LUFT) decision-making parameters, depending on the type sensor or tool used.

The probe can be used in either a “push” or “static” mode to gather a vertical profile at a single time or left in place to gather data over an extended period of time. Sensors can provide electrical resistivity, and pore pressure. Strain gauges measure the forces required to advance the rod tip, allowing indirect determination of the soil type. The data received is a continuous log of the geologic profile at a site and is superior to the current practice of sampling every five feet. Sampling every five feet often results in incomplete characterization of the hydrogeologic conditions at a site.

The cone penetrometer is limited by the presence of cobbles and boulders and generally cannot reach depths of greater than 100 ft below ground surface. Since a majority of California’s LUFT sites are located in regions with a minimum depth to groundwater of less than 50 ft, a cone penetrometer can easily gather information from 5 to 20 locations in a single day. The Department of Defense has made a major commitment to development of this technology and the results of this effort can be leveraged for California’s benefit.

G-1. Laser Spectrometer System

One of the important sensor systems that has been developed for use with the cone penetrometer is a laser spectrometer which can identify a “fingerprint” of fuel hydrocarbons (FHCs). The system takes advantage of the fact that certain substances fluoresce when a particular wave length of light shines on them. The spectral emission as well as the fluorescent lifetime is unique to the substance. The fluorescent intensity indicates the concentration of the substance. As the penetrometer cone is advanced, a neodymium-yttrium aluminum garnet laser pumps light to a dye laser system to induce fluorescence of FHCs. Optical fibers are used to transmit the laser ultraviolet light through the penetrometer rod and a ruby window on the side of the cone. The resulting fluorescent emission light is returned thorough optical fibers to the surface for spectral analysis. The system can provide semi-qualitative and semi-quantitative data on the vertical spatial distribution of FHCs in minutes. The system, while in the demonstration phase, has been tested in the field and with detection limits as low as parts-per-million concentrations of TPH in soils. This sensor system, used in conjunction with the cone penetrometer, holds promise as a relatively inexpensive means to provide needed information about FHC source masses. Concentration data can be provide from a relatively large number of sampling points and source mass can be estimated with increased accuracy.

The use of laser-induced fluorescence with a cone penetrometer is also being tested by the U.S. Navy at the Port Hueneme, California, National Test Site for FHCs. This system is referred to as the Site Characterization and Analysis Penetrometer System (SCAPS). In addition, the SCAPS technology is one of the first being evaluated by the California Environmental Protection Agency for certification. A variety of commercial manufactures have embraced the technology and coupled it with an advanced data visualization system to support informed, real-time field decision making.