California State Water Resources Control Board

Leaking Underground Fuel Tank Guidance Manual

September 2012

CALIFORNIA
Water Boards
STATE WATER RESOURCES CONTROL BOARD
REGIONAL WATER QUALITY CONTROL BOARDS

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Leaking Underground Fuel Tank Guidance Manual

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Chapter 1: Overview of the California Leaking Underground Fuel Tank (LUFT) Guidance Manual

September 2012

Intent of the California LUFT Manual

The intent of the California Leaking Underground Fuel Tank Guidance Manual (CA LUFT Manual, Manual) is to provide guidance to stakeholders and to assist them in making informed decisions regarding the investigation and cleanup of unauthorized releases of fuels from underground storage tanks (USTs) in the State of California. The Manual is designed to guide its users towards solutions for fuel-impacted sites; its contents are user-friendly and "state of the science."

Introduction

The CA LUFT Manual is intended to assist stakeholders involved in the California State Water Resources Control Board (State Water Board) UST Cleanup Program to meet the Program's main objective of protecting human health, safety, and the environment from petroleum products and/or petroleum additives which have leaked from USTs and/or their associated systems. Potential risks to human health and the environment posed by these unauthorized releases of petroleum into the subsurface may include impacts to drinking-water wells, intrusion of vapors into utility lines or buildings, time and costs associated with management of contaminated soil and groundwater during future construction projects, and impacts to nearby surface-water bodies.

Legal.

To mitigate these potential risks, there are four primary sources where the legal requirements for investigation and cleanup of unauthorized releases from USTs are found:

- UST Regulations, California Code of Regulations (CCR) Title 23, Article 5 and Article 11
- Policies and Procedures for the Cleanup and Abatement of Discharges under California Water Code Section 13304 and related State Water Board Resolutions 1992-0049 and 2012-0016
- California Health & Safety Code (H&SC) Sections 25280-25299.8, regarding public health and safety, and safety to the environment while dealing with underground tanks used for the storage of hazardous

While the above documents provide the legal requirements for performing investigation, cleanup, monitoring, and other activities at LUFT sites, they do not provide guidance on the best technical methods to perform these activities in the varied circumstances found at LUFT sites in the real world. This Manual provides information on "state of the science" technologies and implementation strategies that have been proven to be efficient and effective. Regulators, responsible parties (RPs), and consultants are encouraged to utilize this Manual to assist in their decision-making regarding appropriate methods for compliance with regulations and policies at each individual site.

Background

In mid-1985, the Department of Health Services (DHS) and the State Water Board formed a Task Force to establish procedures for determining whether a LUFT site was clean and safe, so as to protect public health and the environment. The procedures were contained in the 1989 LUFT Field Manual.

The statutory authority used to develop the 1989 LUFT Field Manual was the Porter-Cologne Water Quality Control Act, which called for the protection of water with the goal of removing "all" contamination from the soil, surface water, and groundwater affiliated with a site. However, the Task Force recognized "that this goal is unattainable at many sites. Typically, due to the lack of established scientific and technical knowledge, along with limited resources available to the property owner and local, state, and federal government agencies, most cleanup actions cannot achieve a zero contamination level" (State of California 1989).

Because the original Task Force recognized that corrective actions would likely yield some level of residual contamination, the original Task Force developed the following assumptions:

1) "Cleanup of all contaminated soil and dissolved product in groundwater is not always necessary to protect public health and the environment. However, it is desirable to clean up soils and groundwater to the maximum extent practical to reduce any future risk.
2) "All free product floating on groundwater should be removed to the maximum extent practicable, unless neither threat to beneficial uses of water nor danger to residents/workers from fire or explosion exists.
3) "Statewide cleanup levels for contaminated soil and dissolved product are undesirable. Because conditions vary from region to region, the task force decided to develop a general approach that can be used to quickly establish site-specific levels instead of setting state-wide cleanup levels."

The 1989 LUFT Field Manual was intended to provide guidance on the following:

1) Investigating suspected or known leaks at LUFT sites.
2) Assessing risk to human health and the environment when leaks have occurred.
3) Determining cleanup levels in soil, groundwater, and air for contaminated sites.
4) Screening out sites which represent an acceptable degree of risk from further study.
5) Taking remedial actions.

The original 1989 LUFT Field Manual was intended to avoid unwarranted analysis, while ensuring that adequate analysis was performed to identify the extent of contamination problems; more than 20 years later, this Manual has the same intentions.

Scope of the CA LUFT Manual

Much experience, research, and knowledge has been incorporated into the CA LUFT Manual since the development of the 1989 LUFT Field Manual; however, the belief that removal of all contamination is unrealistic is still prevalent. The assumptions that were developed by the LUFT Task Force in 1989 are still applicable in 2012, specifically:

1) Cleanup of all contaminated soil and dissolved product in groundwater is not always necessary to protect human health, safety, and the environment.
2) Free product floating on groundwater should be removed to the extent practicable. State Water Board Resolution 1992-0049 directs that water affected by an unauthorized release attain either background water quality or the best water quality that is reasonable, if background water quality cannot be restored. Any alternative level of water quality less stringent than background must be consistent with the maximum benefit to the people of the state, not unreasonably affect current and anticipated beneficial use of affected water, and not result in water quality less than that prescribed in the water quality control plan for the basin within which the site is located.
3) In Resolution 2009-0042, the State Water Board stated that the issues identified in the resolution are of an ongoing nature and that the State Water Board will take further appropriate action to improve the UST Cleanup Program and the UST Cleanup Fund Program. A State Water Board policy for water quality control that establishes criteria for closure of UST cases that present a low threat to human health, safety, and the environment is necessary for consistency and will facilitate the appropriate closure of UST cases and also improve both the UST Cleanup Program and the UST Cleanup Fund Program.
4) State Water Board Resolution 2012-0016 approved a substitute environmental document and adopted a proposed water quality control policy for low-threat UST case closure on May 1, 2012.
5) The Low-Threat UST Case Closure Policy (Case Closure Policy) became effective on August 17, 2012. This policy is intended to provide direction to responsible parties, their service providers, and regulatory agencies. The Case Closure Policy directs the Regional Water Boards and local agencies to review all cases in the petroleum UST Cleanup Program using the framework provided in this Policy. The Case Closure Policy also seeks to increase UST cleanup process efficiency. A benefit of improved efficiency is the preservation of limited resources for the mitigation of releases posing a greater threat to human and environmental health.

This Manual also has very similar goals as the 1989 LUFT Field Manual did, including: providing guidance on investigating LUFT sites, assessing the risk of an unauthorized release, and employing corrective actions. This version, submitted in September 2012, provides closure criteria for low-threat sites. This Manual is intended for use as a guide for investigation and/or remediation of petroleum and fuel-additive contaminants at LUFT sites which currently or potentially may impact human health, safety, and/or the environment. The Manual is also intended to provide guidance for implementing the requirements established by the Case Closure Policy.

Important! This Manual is **not intended** for use in the investigation or remediation of contaminants other than petroleum and fuel additives.

The Manual is a guidance document; it is intended to work in cooperation with existing regulations.

Due to the diverse nature of the geology and hydrogeology throughout California, this Manual is designed to serve as a general resource document for UST cases throughout the State of California. It does not include information specific to any county or region.

Development of the CA LUFT Manual

The original 1989 LUFT Field Manual was the result of the best collective efforts put forth by local, regional, and state representatives. This Manual is also a collaborative effort but, in addition to local, regional, and state representatives, has included input from the United States Environmental Protection Agency (USEPA) Region 9, RPs, consultants, and the general public. It was important for the State Water Board to give stakeholders an opportunity to play a role in the development of this Manual.

The update process began in 2009 with the State Water Board hosting four public meetings across the state to collect information and ideas for updating the 1989 LUFT Field Manual and to invite discussion on how to improve the overall process of UST investigation and remediation within the state.

Raw input received at each of the four public meetings was consolidated into major topic areas, a Table of Contents was developed, and a wiki site was created to enable interested persons to contribute to the content of the Manual. The wiki site was open for five months, and much information was contributed from stakeholders across California.

Upon closure of the wiki site, Working Groups composed of regulators, consultants, and RPs formed to further refine specific chapters. The Working Groups reviewed the information that had been contributed by the public, filled in details where necessary, and distilled redundant information.

In August 2010, the Draft California LUFT Guidance Manual Version 1.0 was released, reflecting lessons learned and refinements in assessment and corrective action procedures gained since the 1989 LUFT Field Manual. Version 2.0 of the Draft CA LUFT Guidance Manual was released shortly after Version 1.0, in October 2010, with the primary difference between Version 1.0 and 2.0 being updates to the LUFT-Specific Risk Screening Tools. The public was invited to comment on the Draft Manual, and over 400 comments were received. This California LUFT Guidance Manual, submitted in September 2012, reflects the input from the public participation period and also incorporates the consistent statewide case-closure criteria for low-threat petroleum UST sites as required in State Water Board Resolution 2012-0016, the Case Closure Policy. It should be noted that the LUFT-Specific Risk Screening Tools used in Version 2.0 have been replaced by the criteria in the Case Closure Policy.

Content of the CA LUFT Manual

The Manual is separated into three different sections: (1) Administration, (2) Initial Response, Reporting, and Tank Removal, and (3) LUFT Investigation and Remediation. The Manual is written and organized in a manner that encourages stakeholders to access the relevant information for which they are looking rather than requiring them to read the Manual cover to cover.

Section 1: Administration

This section of the Manual includes information on the maintenance, performance, organization, and management of the State Water Board UST Cleanup Program. It includes information such as the roles and responsibilities of parties, a summary of the UST Cleanup Fund Program, how to use the State Water Board's GeoTracker database, and provides guidance on how to proper develop work plans and reports.

Section 2: Initial Response, Reporting, and Tank Removal

This section discusses the types of responses needed at LUFT sites based on the threat to human health, safety, and the environment. It also discusses initial reporting and abatement procedures, and proper tank removal.

Section 3: LUFT Investigation and Remediation

This section discusses the fate and transport of petroleum in the subsurface, the crucial process of conceptualizing a LUFT site to make decisions, the investigation of soil, water, and soil vapor including proper laboratory analysis, the risk evaluation and management associated with LUFT sites, and remedial actions.

References

State of California. 1989. Leaking Underground Fuel Tank (LUFT) Task Force. LUFT Field Manual. Guidelines for Site Assessment, Cleanup, and Underground Storage Tank Closure. October.

California State Water Resources Control Board (State Water Board), Resolution 2012-006, Low-Threat UST Case Closure Policy. Adopted May 1, 2012, effective August 17, 2012.

Section 1: Administration

Chapter 2: Roles and Responsibilities

September 2012

Scope of This Chapter

This chapter describes the roles and responsibilities of parties involved in leaking underground fuel tank (LUFT) sites throughout the State of California.

There are three primary parties involved in the investigation and remediation of LUFT sites: the responsible party (RP), the RP's authorized agent or consultant, and the lead regulatory agency overseeing the case. Each party has different roles and responsibilities, as discussed in this chapter. This chapter provides information on the *chief* roles and responsibilities of each primary party, but does not list all possible roles and responsibilities.

Other stakeholders who may be involved in LUFT sites are adjacent property owners, the California Underground Storage Tank (UST) Cleanup Fund (Fund), the community, real-estate developers, etc.

Responsible Party

According to the California Code of Regulations (CCR), Title 23, Division 3, Chapter 16, Article 11, Section 2720, "Responsible party" means one or more of the following.

- Any person who owns or operates a UST used for the storage of any hazardous substance; there is an implied nexus requirement (must be the owner or operator at the time of the release).
- In the case of any UST no longer in use, any person who owned or operated the UST immediately before the discontinuation of its use; "no longer in use" does not require temporary or permanent closure; UST can still contain product, but the new owner and operator must have no use for it.
- Any owner of property where an unauthorized release of a hazardous substance from a UST has occurred and any landowner that owned at the time of, or following, the unauthorized release, until the site is cleaned up, regardless of whether owner caused or contributed to the release.
- Any person who had or has control over a UST at the time of or following an unauthorized release of a hazardous substance and any person who has legal control over the source of the release and the ability to obviate the condition. (Example: Lessees)

Note: Easement holders generally not RPs (not enough "control")

Legal Standard: Name a party as an RP if a local agency has reasonable and credible evidence to indicate a person meets the definition of a responsible party.

In addition, an RP may be designated a secondary responsible party if the primary RP is performing corrective action, and the RP requesting secondary status did not initiate or contribute to the actual discharge. However, the secondary RP may become a primary RP when the other primary RP fails to perform corrective action.

California Health & Safety Code (H&SC), §§25280-25299.8 (regarding hazardous substances and waste stored in underground locations) and CCR Title 23, Division 3, Chapter 16, "Underground Storage Tank Regulations," refer to the RP as "owner" and/or "operator."

"Owner" is defined in the California H&SC as "the owner of an underground storage tank" and "Operator" is defined as "any person in control of, or having daily responsibility for, the daily operation of an underground storage tank."

In the following sections, "RP" will be used interchangeably with "owner" and "operator."

The RP is responsible for complying with California H&SC §§25280-25299.8 and Articles 5 and 11 of the CCR, "Underground Storage Tank Regulations." The RP's chief legal responsibilities are to comply with the California H&SC and CCR Articles 5 and 11, which include:

- Taking corrective action in response to any unauthorized release, which includes abatement, preliminary site assessment, and investigation.

- Reporting unauthorized releases from any UST with secondary containment and spills or overfills which the owner or operator is unable to clean up or which is still under investigation to the regulatory agency within eight (8) hours of detection.
- Providing an initial report of an unauthorized release from a UST to the local agency within 24 hours and transmitting additional information regarding an unauthorized release to the local agency on a written form or using an electronic format developed by the State Water Resources Control Board (State Water Board) within five working days.
- "Claim" the site or authorize an agent to do so on the RP's behalf on the State's LUFT tracking database, GeoTracker (see GeoTracker – Stakeholder Responsibilities). Provide a list of all current record owners of fee title of the site to the lead agency under H&SC §25297.15.
- Notify all impacted property owners of the proposed Corrective Action Plan (CAP) and proposed closure.

The State of California retains the right to enforce penalties against the RP(s) if action is not taken or if the nature of the release is severe enough to warrant such action. Funding for clean-up activities may be available through the Fund for selected LUFT sites via reimbursement of submitted invoices. The UST Cleanup Fund chapter describes this process in greater detail.

State laws outline a regulatory structure that allows an RP to conduct the necessary site investigation and perform corrective actions in a timely and cost-effective manner.

RPs often contract with third-party environmental consultants to assist in the investigation and evaluation of a LUFT site. RPs are encouraged to work with reputable firms and to properly manage consultants to keep costs under control, ensure that established regulatory agency deadlines are responded to on time, and have a clear understanding of the project objectives. Federal and state laws require every owner or operator of a petroleum UST to maintain financial responsibility to pay for any damages arising from operation of that UST. The roles and responsibilities of the consultant are discussed below.

Further Reading.

Helpful resources regarding the definition of an RP are:

State Water Board. 2006. "Notice of Responsibility for Corrective Action at Local Oversight Program Sites." May.

State Water Board. 1994. "Primary/Secondary Responsibility for Tank Cleanups." September 22.

State Water Board. 1994. "UST Local Oversight Program, Responsible Party Definition." July 26.

State Water Board. 1994. "Clarification of the Definition of Responsible Party under the Corrective Action Regulations." January 25.

Consultant

The consultant is defined as a third party, a licensed and experienced professional geologist or civil engineer, hired by an RP to perform tasks associated with the investigation and remediation of a LUFT site. The intent of hiring a licensed professional is to ensure that the work required at a LUFT site is performed in accordance with the California Business and Professions Code (BPC) and other applicable laws and regulations. The consultant should address the contamination from a scientific perspective, within the legal framework of the LUFT program, and on behalf of the RP. In practice, consultants should make every effort to meet regulatory requirements in a cost-effective manner. It is important to note that, even though the regulatory agency may largely interact with the consultant, any directives issued by the regulatory agency are officially addressed to the RP. Non-compliance enforcement is also ultimately directed to the RP; however, RPs rely on consultants to meet their legal responsibilities, which are discussed in the RP section above.

Often, consultants are responsible for ensuring that field work is conducted in accordance with federal and state law. For further information, see the Health and Safety chapter of this Manual.

It is recommended that RPs sign contracts with reputable firms or individuals who have experience in LUFT investigation, risk evaluation, remediation, and site closure to protect an RP from paying too much for unnecessary work or from having to request addenda to work plans which were deemed “incomplete” or “not acceptable” by the regulatory agency.

Regulatory Agency

A regulatory agency is any agency authorized to implement, administer, and enforce regulations. The regulatory agencies are responsible for representing the people of California. The agencies with a role in this program include the State Water Board, the nine Regional Water Quality Control Boards (Regional Water Boards), county-level Local Oversight Programs (LOPs), and county or city Local Implementing Agencies (LIAs).

Agency Jurisdiction

Based on the nature of the LUFT release and its impact on human health, safety, and the environment, different types of agencies have jurisdiction over regulation of the site and, in some cases, jurisdiction is shared between agencies, Regional Water Boards and local agencies, LOPs, and LIAs.

The State Water Board and Regional Water Boards are responsible for protecting beneficial uses of water. Beneficial uses, which can be actual or potential, include municipal water supply, recreation, industrial water supply, and agricultural water supply. Therefore, the State Water Board and Regional Water Boards have jurisdiction over cases where there is a potential to impact groundwater quality or where groundwater quality has already been affected. The regulatory agency responsible for oversight of corrective actions at LUFT sites can be a Regional Water Board, a county agency contracted by the State Water Board to administer the LOP, or an LIA with the authority to oversee corrective actions at LUFT sites not under an LOP contract. Regional Water Boards and LOP agencies have authority to oversee corrective actions at any site under their jurisdiction. Some LIAs, with Regional Water Board approval, can oversee corrective actions, while others oversee actions related only to soil contamination and must refer cases that involve groundwater to the Regional Water Board.

LOPs, mostly county health or fire departments including divisions such as environmental health, occupational health, and hazardous materials management, are contracted with the State Water Board (some since as early as 1988) under Resolution 1988-0023 to provide oversight of LUFT cases, and are responsible for cases related only to soil contamination (“soils only” cases), as well as groundwater contamination cases.

Where an LOP exists, the LOP is the lead agency for sites within the LOP’s geographic boundaries and the Regional Water Board provides technical support when needed, while the State Water Board handles any petitions regarding LOP actions or inactions. For example, if there is a conflict of opinion between the consultant and the LOP case worker, there can be a formal request for a meeting to address concerns or issues. A formal letter request should be submitted to the Regional Water Board case worker or supervisor, usually uploaded to the case page on GeoTracker. The LOP should be copied on the message as well, and the discussion of the issues should proceed.

LIAs are county, city, or other political or municipal (i.e., water) districts and often include divisions such as environmental and occupational health, fire, building/planning/redevelopment, and hazardous materials management. Some regulate USTs as a Certified Unified Program Agency (CUPA) and may supervise soil and groundwater remediation, while fire departments and hazardous materials management offices also have responsibility for fire and explosion prevention/ control at LUFT sites. Thus, local agencies usually have primary responsibility for inspection, leak detection, closure, and fire/public safety. In many instances, these agencies only supervise “soils only” LUFT cases. The LIAs are not under a contractual obligation to a Regional Water Board or the State Water Board. If there is a conflict of opinion between the consultant and the LIA case worker, a request may be made to meet with the LIA case worker’s supervisor. If there is no resolution or willingness to discuss the issue, the matter may need to be decided in the courts.

At times, agreements between local agencies and Regional Water Boards are established to allow local agencies regulatory authority over limited-extent, groundwater-remediation LUFT cases. Regional Water Boards have the authority to supervise remediation at sites referred by local agencies and to provide approval for closure on cleanup cases where water quality is affected or threatened. If there is a conflict of opinion with a Regional Water

Board case worker, an RP has the following two options. First, the RP may request a meeting with the case worker's supervisor, in an attempt to resolve the issues at that level. Second, the RP may request the State Water Board to review the differences. This is allowed under Resolution 1992-0049, as amended by Resolution 1996-0079; these resolutions deal with case closure. If the issues include a technical disagreement (for example, deciding on the number of monitoring wells and where to install them, or selecting which remedial system to install), the conflict must be resolved at the local level.

Regulatory Agency Responsibilities

The role of these agencies is to verify that RPs follow applicable laws and regulations throughout the investigation and selected remediation processes.

Regulatory agencies' primary legal responsibility is to ensure compliance with the California H&SC, Porter-Cologne Water Quality Control Act, and CCR Title 23, Division 3, Chapter 16:

- Review and concur with or reject work plans for assessment, monitoring, and remedial activities
- Review and receive or deny electronic submittals of information uploaded by RPs into GeoTracker (see GeoTracker)
- Issue directives and enforcement letters to RPs
- Ensure that cases are moving through the LUFT cleanup process toward closure in an effective and timely manner

Each corrective action required by a regulatory agency must be described in a work plan submitted by the RP. The regulatory agency is responsible for reviewing and approving all work plans prior to their implementation. Regulatory agencies are also responsible for reviewing all reports related to the required corrective actions at all sites under their jurisdiction. Additionally, regulatory agencies may require prior notice before any field work is conducted at a cleanup site, and they have the authority to be present during any field work. Regulatory agencies have the authority to reject analytical or field results obtained during field work if the proper inspection arrangements have not been made and there is a reasonable suspicion that the data are not valid. At times, regulatory agencies may require notice of UST inspection and remediation inspection, at a minimum of three business days (or other agreed-upon interval among RP, consultant, and regulatory agency).

Legal.

State Water Board Resolution 2012-0016 approved a substitute environmental document and adopted a proposed water quality control policy for low-threat UST case closure on May 1, 2012. The Low-Threat UST Case Closure Policy (Case Closure Policy) became effective on August 17, 2012 and established consistent statewide case closure criteria for low-threat petroleum UST sites. The Case Closure Policy is intended to provide direction to RPs, consultants, and regulatory agencies on the parameters that constitute a low-threat site. The Risk Evaluation and Risk Management Chapter provides a summary of the parameters. Annually, or at the request of the RP or party conducting the corrective action, the regulatory agency shall conduct a review to determine whether the site meets the criteria contained in the Case Closure Policy.

Cases that meet the criteria in the Case Closure Policy do not require further corrective action. If the case has been determined by the regulatory agency to meet the criteria in this policy, the regulatory agency shall notify RPs that they are eligible for case closure and, if applicable, complete all notification requirements, monitoring well destruction, and waste removal, prior to issuance of a uniform closure letter consistent with H&SC §25296.10.

Public Participation

According to CCR Title 23, Division 3, Chapter 16, Article 11, Section 2728, the regulatory agency with jurisdiction over a LUFT case must inform the public about each confirmed unauthorized release that requires corrective action. H&SC §25356.1 also requires the regulatory agency to involve the public in site cleanup decisions. The public may be made aware of the proposed activities contained in the corrective action in at least one of the following ways:

1) Publication in a regulatory agency meeting agenda;
2) Public notice posted in a regulatory agency office;
3) Public notice in a local newspaper;
4) Block advertisements;
5) Public service announcement;
6) Letters to individual households; or
7) Personal contact with the affected parties by regulatory agency staff.

Information regarding the corrective action of a case is generally made available to the public once the site has been created in GeoTracker (see GeoTracker chapter). The site in GeoTracker will also include information on how the public can submit comments and also provide the deadline for comments.

Upon the completion of the corrective action, the regulatory agency shall give public notice if both of the following situations exist:

1) Implementation of the CAP does not achieve the cleanup levels established in the CAP; and
2) The regulatory agency does not intend to require additional corrective action, except for monitoring.

The regulatory agency shall comply with all applicable provisions of the California Environmental Quality Act (CEQA), Public Resources Code, commencing with §21000. LUFT sites are generally exempt from other CEQA requirements.

Other Stakeholders

Other stakeholders have a role in LUFT cases. The adjacent property owners may have an interest because their property/ies may potentially be contaminated. Community members may be interested because they want to know whether there are health and/or environmental risks to their community. Real-estate developers may have an interest when they have prospective projects planned for the site. Public meetings can be held with these stakeholders before a CAP is agreed on.

Chapter 3: UST Cleanup Fund

September 2012

Scope of This Chapter

This chapter describes the Underground Storage Tank (UST) Cleanup Fund Program and explains its purpose, history, and applicability to UST sites in the State of California. This chapter is written for an audience with no prior knowledge of the Fund and is meant to aid responsible parties (RPs), consultants, and state and local regulators in their work on Leaking Underground Fuel Tank (LUFT) sites throughout the State of California.

The Barry Keene Underground Storage Tank Cleanup Fund Act of 1989 created the UST Cleanup Fund (USTCF, also known as “the Fund” – these terms will be used interchangeably in this document) to help owners and operators of USTs satisfy federal and state financial responsibility requirements. The Fund is administered by the Division of Financial Assistance (DFA) of the California State Water Resources Control Board (State Water Board) as a means of assisting UST owners and operators in meeting federal and state corrective-action requirements.

The USTCF’s mission is to contribute to the protection of California’s public health and water quality through (1) establishing an alternative mechanism to meet financial responsibility requirements for owners and operators of petroleum USTs, and (2) reimbursing eligible corrective action costs incurred for cleanup of contamination resulting from the unauthorized release of petroleum from USTs. The Fund Regulations have been revised periodically in response to new legislation and to address issues not anticipated when the initial Fund regulations were written.

Statutes and Regulations

To fulfill the federal financial responsibility requirements specified in 40 *Code of Federal Regulations* (CFR), Part 280(H), the Fund is available to assist many thousands of individuals, small businesses, and corporations in meeting costs for the cleanup of contaminated soil and groundwater caused by leaking petroleum USTs. The federal financial responsibility requirements also require the Fund to provide coverage for third-party liability due to unauthorized releases of petroleum from USTs.

In addition to tank operators and owners, the Fund provides money to the Regional Water Quality Control Boards (Regional Water Boards) and Local Oversight Programs (LOPs) to abate emergency situations or to clean up abandoned sites that pose a threat to human health, safety, or the environment as a result of unauthorized petroleum releases from USTs.

Legal.

The statutory authority for operation of the Fund and affiliated programs is contained in the California Health & Safety Code (H&SC), Chapters 6.75, 6.76, and 6.77. The most recent version of these code sections is dated January 2010.

The Fund regulations are contained in the California Code of Regulations (CCR), Title 23, Division 3, Chapter 18 (commencing with Section 2803). The current version of the Fund regulations is dated August 5, 2004.

UST Cleanup Fund staff members review reimbursement, budget, and pre-approval requests in accordance with the requirements of Section 2808.2(b) of the UST Cleanup Fund Regulations, CCR Title 23, Division 3, Chapter 18.

Established by Senate Bill (SB) 299 in 1989, the USTCF statutes require every owner of a petroleum UST that is subject to regulation under H&SC Chapter 6.7 to pay a per-gallon storage fee. In recent years, the Fund has received up to $320 million annually from storage fees, of which up to $260 million were available to reimburse eligible claimants for the costs of ongoing UST cleanups at 4,600 sites.

The maximum amount of reimbursement per unauthorized release occurrence is $1.5 million, minus any deductibles or settlement adjustments. The deductible amounts are set by statute and range from $0 to $40,000, based on the priority class of the claimant and any UST permit waivers. Since the USTCF's inception in the early 1990s, over $3.1 billion have been reimbursed to eligible UST owners and operators to clean up soil and groundwater contamination in the State of California.

In the fall of 2007, an external Fund Stakeholder Review group was convened to discuss whether the Fund should be extended and, if so, whether any potential Fund improvements recommended by legislation, regulation, or internal procedure would be adopted. After several meetings, the participants agreed that the Fund should be extended for 10 years and that the current fee ($0.014 per gallon) should not be changed. Following the 2007 review, a Consensus Report was prepared and distributed. In February 2008, legislation was introduced proposing the extension of the Fund. On September 30, 2008, the bill (SB 1161, Lowenthal) was signed by the Governor, extending the Fund until January 1, 2016.

Legal.

On May 19, 2009, the State Water Board passed Resolution No. 2009-0042. This resolution initiated a series of reviews of the Fund, including the UST Cleanup Program. One of the requirements of this resolution was that a Task Force be created to make recommendations for improvements to the USTCF administrative procedures and to improve the UST Cleanup regulatory program. As a result, an audit was conducted at the Fund.

More information on the Task Force created to make recommendations for improvements to the Fund and results of the audit can be found on the Fund's website:
http://www.waterboards.ca.gov/water_issues/programs/ustcf/taskforce.shtml

In February 2011, legislation was introduced proposing various changes to existing law pertaining to the cleanup of leaking USTs. Among its provisions, the bill: (1) required Regional Water Boards and local agencies with responsibility for overseeing the cleanup of leaking USTs to submit specified information on each UST site to the State Water Board electronically; (2) required UST owners and operators to submit information regarding the unauthorized release to local agencies in a format specified by the State Water Board; and (3) authorized the State Water Board to close UST sites (and thereby discontinue requirements for further cleanup) that are under the jurisdiction of a local implementing agency (LIA), upon petition by a UST owner/operator or as part of its regular review of UST sites that have been open for more than five years. LIAs are local agencies who oversee the cleanup of leaking USTs without contract or oversight by the State Water Board. The bill also modified eligibility requirements for the Fund, to allow UST owners who are directed by a federal agency to clean up leaking USTs to be eligible for reimbursement from the Fund. Under prevailing law, UST owners were only eligible to be reimbursed from the Fund if they were directed by a Regional Water Board or local agency to clean up a site. On October 8, 2011, the bill (AB 358, Smyth) was signed by the Governor.

Fund Cost Guidelines

The Fund Cost Guidelines have been developed pursuant to H&SC Section 25299.57(h). This summary of expected costs may be used by claimants as a guide in selecting and supervising consultants and contractors:
http://www.waterboards.ca.gov/water_issues/programs/ustcf/docs/cost_guidelines/costguidelines.pdf.

The primary purpose of the Fund Cost Guidelines is to provide direction to claimants for evaluating proposed and incurred corrective action costs at sites eligible for participation in the Fund. Specifically, these guidelines are intended to help claimants identify reimbursable goods and services and understand how the Fund evaluates activities and costs. The guidelines are also intended to assist claimants in judging whether additional justification will likely be required to support given costs, or whether a call for assistance from the Fund is in order.

The guidelines do not establish reimbursement limits for the listed items and activities. They are not intended to remove the element of competition or freedom of choice from the industry, meaning that competitive bidding for work performed at a LUFT site is encouraged.

5-Year Review

H&SC Section 25299.39.2(a) requires the Fund to review the case history of each claim having a Letter of Commitment (LOC) active for more than 5 years annually, unless the owner or operator objects to the review. This is known as the 5-Year Review.

The purpose of the 5-Year Review is to determine whether a recommendation for case closure is in order, or whether alternative actions are appropriate. Aside from being required by law, this review is beneficial because it provides for an additional party to check on the progress of the case relative to the expenditure of funds and reduces the chance that the responsible party (RP) will run out of funds before the site is cleaned up. It also provides an opportunity for the Fund to track cases and better facilitate work to achieve site closure.

The Fund's 5-Year Review Unit reviews site case history and directives to make one of the following recommendations:

1) Recommend the site for closure.
2) Concur with the current corrective-action activities.
3) Recommend modification to the current corrective action(s).

The Fund's 5-Year Review Unit reviews site case history and may request information from the regulatory agency, generally by scheduling an appointment to review the case file. By requesting information from the agency, the 5-Year Review Unit can verify that there is no additional information other than what is available in GeoTracker; if there were, such information could potentially change recommendations.

The 5-Year Review is issued first to the regulatory agency, which is given 45 days to respond prior to submittal of the 5-Year Review to the RP. This procedure is both a courtesy and a preventive measure, with the expectation that any errors will be noted and corrected, so that the regulatory agency will not be approached by the RP, inquiring as to which recommendations to follow: those in the 5-Year Review or those issued by the regulatory agency. Concurrent with submittal to the RP, the review is uploaded to GeoTracker as a public document. The 5-Year Review Unit has been internally required to upload 5-Year Reviews to GeoTracker since May 2009.

It is the responsibility of the RP to respond to the recommendations made and provide a path forward based on the recommendations. If closure is warranted, it is recommended that the RP or RP's consultant assemble a comprehensive closure-request package for submittal to the lead regulatory agency. See the Reports chapter for information necessary in a Case Closure Request Report. Additionally, the RP may petition the SWRCB for a review of its case if the RP feels that corrective action for the site has been satisfactorily implemented, but that closure has been nevertheless denied. It is strongly recommended that the RP or RP's consultant communicate as completely as possible with the regulatory agency to resolve issues but, as a last resort, the RP may petition the SWRCB for review of the case. See more information regarding closure petitions in the Help Box of this chapter.

Cost Pre-Approval

The Fund has historically pre-approved estimated corrective action costs to ensure that costs are eligible, reasonable, and necessary. Cost pre-approval was suspended in 2003 due to Fund staffing reductions, and was resumed in fiscal year (FY) 2006-07.

During 2010, cost pre-approval was converted to a budget-approval process in which budgets are established for all planned activities for a claim covering a 12-month period. Fund technical staff place each active Priority A, B, and C claim in a budget category. The budget format is structured around eight standard work phases, applicable sub-tasks for each phase, and projections for all activities to be conducted during each quarter. For efficiency in processing, reimbursements are structured to directly correlate with the eight standard work phases in the budgets.

As currently structured, for each new FY, the Fund will assign a budget allotment amount to each budget category. For sites at which a remedial system is starting up, already in operation, or getting ready for closure, a consultation process will occur between the Fund, the regulator, the consultant, and the claimant before any work is conducted or any money is spent. This process is intended to ensure that everyone agrees on the scope of work for a given claim. Finally, for all budget categories, it will be required that all activities proposed in the budget fit into the overall road map to closure, based on the most current conceptual site model (CSM; see Conceptual Site Model chapter).

GeoTracker

Fund payment information is uploaded to GeoTracker (SWRCB's environmental database), including the "CUF Claim #," "CUF Priority Assigned," and "CUF Amount Paid." The "Clean-Up Fund Payment Report" in GeoTracker includes the total requested amount, paid amount, and date received for each payment. Most payments listed also include the "Clean-Up Fund Payment Detail Report," which describes detailed invoice information and comments, if needed. See the GeoTracker chapter for more information on this database.

Help! For more information about how to file a closure petition or other UST-related petition, go to:
http://www.waterboards.ca.gov/water_issues/programs/ust/cleanup/petitions.shtml

For the most recent update on the availability of funding, refer to:
http://www.waterboards.ca.gov/water_issues/programs/ustcf/paymentformsinfo.shtml

The Fund website also has materials for Pre-Approval requests, including the necessary forms and instructions. To submit a Pre-Approval request (for preparation of a case closure request report) or for other related activities, see:
http://www.waterboards.ca.gov/water_issues/programs/ustcf/docs/cost_preapproval/costpreapproval.pdf

Further Reading.

Each FY, the Fund prepares a "Legislative Annual Report," which provides a performance summary of the Fund's activities. This information comes from the previous FY's status on claims received and reimbursed, in addition to other historical data. This report also provides a useful summary of the major legislative changes to the Fund from its inception.
http://www.waterboards.ca.gov/water_issues/programs/ustcf/legannualreports.shtml

References

USTCF (the Fund) website:http://www.waterboards.ca.gov/water_issues/programs/ustcf/

Chapter 4: GeoTracker

September 2012

Scope of This Chapter

This chapter presents GeoTracker, the State Water Resources Control Board (State Water Board) database, and explains its required use in the cleanup process of Leaking Underground Fuel Tank (LUFT) sites. It describes the history behind the development of GeoTracker, and the goals associated with GeoTracker's use. The responsibilities of various relevant parties are defined with regard to GeoTracker.

Background

GeoTracker is an on-line database and geographic information system (GIS) that 1) provides access to statewide environmental data and 2) tracks regulatory data for the following types of sites:

- LUFT cleanup sites,
- Cleanup Program Sites (CPS; also known as Site Cleanups [SC] and formerly known as Spills, Leaks, Investigations, and Cleanups [SLIC] sites),
- Military sites (consisting of: Military UST sites; Military Privatized sites; and Military Cleanup sites [formerly known as Department of Defense non-UST]),
- Land Disposal sites (Landfills),
- Permitted UST facilities, and
- Other groundwater data from the Groundwater Ambient Monitoring Assessment (GAMA) Program, sites with Waste Discharge Requirement (WDR) permits, and farm lands.

Legal.

AB 2886 (Ch. 727, Stats. of 2000), authorized the State Water Board to establish electronic formats for reporting compliance data.

On September 30, 2004, the State Water Board adopted regulations (Chapter 30, Division 3 of Title 23, California Code of Regulations [CCR], and Division 3 of Title 27, CCR) which required electronic submittal of information (ESI) for LUFT, SLIC, DOD, and Landfill groundwater cleanup programs. These regulations also added new Data Dictionaries (the format for electronic data submittals) to CCR Title 27, in coordination with existing California Environmental Protection Agency (Cal/EPA) Unified Program Data Dictionaries.

Additionally, Section 3894 of CCR outlines the timing of electronic reporting requirements. As of January 1, 2005, soil and water chemistry analytical data, and well data included in compliance reports, must be electronically submitted. Beginning July 1, 2005, submittal of a complete copy of all required reports, in PDF format, into GeoTracker replaced the paper copy reporting requirements (paperless reporting).

AB 358 (Ch. 571, Stats. of 2011) requires that the owner or operator transmit additional information regarding an unauthorized release to the lead regulatory agency on a written form or using an electronic format developed by the State Water Board.

Purpose of GeoTracker

The purpose of GeoTracker is to allow interested parties to obtain electronic data, and textual and graphical information about various facilities and sites with groundwater quality concerns. GeoTracker provides on-line tools to analyze potential threats to drinking-water sources. Additionally, GeoTracker has a graphical user interface that allows quick access to facility and site information over the Internet.

GeoTracker has both public and secure pages/screens:

- http://geotracker.waterboards.ca.gov (public)
- https://geotracker.waterboards.ca.gov/regulators (regulators - secure login page)

- https://geotracker.waterboards.ca.gov/esi (responsible parties [RPs] and/or their agents - secure login page)

Benefits of Electronic Reporting

The implementation of electronic reporting has provided benefits for both the regulatory agencies and the public. Electronic reporting:

- Provides decision-makers with accurate, up-to-date, accessible, and complete statewide information concerning cleanup sites where there has been an unauthorized release of contaminants.
- Enhances the capabilities of the U.S. Environmental Protection Agency (USEPA), State Water Board, Regional Water Quality Control Boards (Regional Water Boards), and local regulatory agencies in monitoring and assessing the contaminant threat to drinking-water wells.

Facilitates public access to information: Limits the need for interested parties to physically travel to a government building to review a paper copy of the case file. Concerned individuals can review and analyze available information over the Internet.

Chapter 4: GeoTracker
Electronic Submission of Information

September 2012

Laboratory Data

Analytical data (including geochemical data) for all soil, vapor, and water samples collected for the purpose of subsurface investigation or remediation are required to be uploaded into GeoTracker in the specified Electronic Deliverable Format™ (EDF) described at:

http://www.waterboards.ca.gov/ust/electronic_submittal/docs/edf_gr_v1_2i.pdf

The EDF is a comprehensive data standard designed to facilitate the transfer of electronic data files between data producers and data users. Laboratories can produce the electronic data deliverable (EDD) in specified Electronic Deliverable Format™ (hereafter referred to as EDF) through their Laboratory Information Management System (LIMS) software or by using the U.S. Army Corps of Engineers Loading Tool (COELT) software.

The EDF components for laboratory data include:

- Chain-of-Custody Information
    - Sample collection information
    - Administrative information
    - Preservatives added to the samples
    - Conditions of transport
- Laboratory Results Information
    - Tests performed
    - Parameters tested
    - Analytical results
- Quality Assurance (QA) Information (key to data verification)
    - Detection limits
    - Control limits for precision and accuracy
    - Narrative report explaining non-conformances
- Built-in Guidelines and Restrictions
- Valid Value Lists (VVLs)

Compliance Reports

Compliance Reports for contaminated soil, soil-gas, or groundwater sites are required to be uploaded to GeoTracker in PDF format. These reports should include the signed transmittal letter, professional certification, and all collected data.

Boring Logs and Well-Screen Intervals

Boring logs prepared by an appropriately registered professional must be uploaded into GeoTracker in PDF format. If a monitoring well is installed, the screen depth (measured in feet from the top of casing to the top of the screened interval) and the length of the screened interval (also in feet) must be entered into GeoTracker when the well is added as a new Field Point Name to the site's online list of Field Point Names.

Depth-to-Water Data

Depth-to-water information for monitoring wells (the measured depth from the top-of-well-casing to the groundwater surface, reported to the nearest hundredth [0.01] of a foot) must be uploaded to GeoTracker whenever the data are collected, even if the well is not sampled during a given sampling event. Drinking-water wells generally do not need to have their depths to water reported unless they are surveyed as permanent sampling points (a "permanent sampling point" is defined as a well location that is sampled for more than a 30-day period).

Locational & Elevation Data

If samples from permanent sampling points are included in a report to a regulatory agency as part of a cleanup program, the geographic latitude and longitude of these sampling-point locations must be surveyed to sub-meter accuracy. These locations typically include any groundwater or similar monitoring points at the site or any drinking-water wells that are included in the regulatory report. The surveyed locational coordinates for these permanent sampling points must be uploaded to GeoTracker in the North American Datum of 1983 with longitude and latitude measured in decimal degrees, reported to 7 decimal points, and longitude expressed as a negative number to indicate degrees west of the Prime Meridian. Transient or one-time sampling points (e.g., direct-push technologies, piezometers, grab samples, soil borings, stockpile samples, etc.) do not need to be surveyed.

The elevation at the top-of-casing for all permanent groundwater monitoring wells must be uploaded to GeoTracker. Drinking-water wells included in the report do not need to have top-of-casing elevation reported unless they are identified as permanent sampling points (i.e., are sampled for more than a 30-day period). For permanent sampling points, the top-of-casing elevation must be surveyed to 0.1-foot accuracy to the vertical datum and within 0.01 foot of each permanent sampling point at the site.

Permanent sampling points must be surveyed by a California Registered Civil Engineer or licensed professional surveyor. See Site Assessment Chapter, Well Survey section for further details.

Site Map

An electronic, generalized site plan map must be uploaded to GeoTracker. The site map should display buildings, tank locations (including former tank locations), dispenser islands, streets bordering the facility, monitoring well locations, boreholes, and all other sampling locations where soil, water, and vapor samples have been collected. The site map is uploaded as a stand-alone document and may be submitted in GIF, TIFF, JPEG, or PDF format. Additional updated site maps may be submitted at any time as additional activities are completed, but at a minimum, whenever new field points are associated with the site.

Help! The process of how to format and upload data and other technical information can be found under the "Electronic Submittal of Information" links at http://www.waterboards.ca.gov/ust/electronic_submittal/index.shtml.

Chapter 4: GeoTracker
Stakeholder Responsibilities

September 2012

Non-Regulatory Stakeholders

Responsible Party (RP)

RPs have two primary electronic reporting responsibilities: 1) "claiming" their site(s) in GeoTracker, meaning the RP takes responsibility for the uploading of required documentation, and 2) uploading all ESI compliance data and reports that have been completed since AB 2886 was adopted (see Legal box). If the RP chooses not to upload ESI compliance submittals personally (typically, the RP does not do the uploading), the RP may delegate all or a portion of the upload duties to an "Authorized RP Agent" and/or may grant secondary upload access to Contractors and/or Laboratories. Only RPs and Authorized RP Agents can grant secondary access to Contractors and Laboratories.

In order to claim a site, the RP (or an Authorized RP Agent acting on the RP's behalf) must create a GeoTracker account by submitting a Password Request, if the RP (or Authorized RP Agent) doesn't already have one. The RP (or Authorized RP Agent) then logs onto the relevant GeoTracker account and searches for the site using the "Request Additional Facilities" option. Once the site is found, the RP (or Authorized RP Agent) places a checkmark in the "Add" box and clicks on "Request Checked Facilities" to request the site. (**Note:** After requesting the site, Authorized RP Agents must also email or fax a signed Authorized RP Agent Form to the State Water Board). The Authorization Form can be found in the "Getting Started" section on the public ESI page (http://www.waterboards.ca.gov/ust/electronic_submittal/index.shtml) (instructions are available in the GeoTracker Beginner's Guide). If additional assistance is needed, the GeoTracker Help Desk can be contacted via email at: geotracker@waterboards.ca.gov or toll free via telephone at (866) 480-1028.

Once the State Water Board has approved the request for the site by the RP or their Authorized RP Agent, the RP will have successfully met the prerequisite regulatory compliance requirement to "claim" the site.

Important! For all open cases, timely upload of all responses to corrective action requests and of all other required electronic submittals **is required by law**. Corrective action responses are not considered complete until all required electronic submittals have been uploaded. The RP is out of compliance if the open case is not claimed in GeoTracker and the required information is not uploaded into GeoTracker; this can make a UST Cleanup Fund (Fund) site ineligible for reimbursements until that site is brought into compliance with GeoTracker data requirements and, in addition, non-compliance with State regulations can result in fines being assessed in accordance with but not limited to Section 13327 of the California Water Code (WC). The RP is ultimately responsible for making sure that an open case is in regulatory compliance.

Legal.

Section 13327 of the California WC describes the conditions to assess and determine fines based on Administrative Civil Liabilities. According to Section 13350 of the WC, the State Water Board or Regional Water Board may impose civil liability fines either on a daily basis or on a per-gallon basis, but not both. The civil liability on a daily basis shall not exceed $5,000 for each day the violation occurs and shall not be less than $500 for each day in which the discharge occurs and for each day the cleanup and abatement order is violated. The civil liability on a per-gallon basis shall not exceed $10 for each gallon of waste discharged.

Authorized RP Agent

An Authorized RP Agent is typically an environmental consulting firm whom the RP has designated to act on his or her behalf in fulfilling the RP's GeoTracker electronic reporting responsibilities. An RP can still create a personal GeoTracker RP account even if he or she chooses to designate an Authorized RP Agent to act on his/her behalf.

If they so choose, Authorized RP Agents can do all of the required ESI compliance uploading on behalf of an RP without requesting Contractors or Laboratories to perform uploads. Instructions for claiming a site on behalf of the RP are under the "Responsible Party" section above.

Contractor

An RP (or an Authorized RP Agent) may employ a number of Contractors to collect samples, perform groundwater measurements, survey locations and elevation, upload data and compliance reports, and manage data for facilities or cleanup sites. To gain access to an RP's GeoTracker site, a Contractor logs onto their GeoTracker "Contractor" account, and requests access to the site (the RP or Authorized RP Agent must already have successfully "claimed" the site for this process to function). After the Contractor requests access to the site, the RP (or Authorized RP Agent) must then log onto his or her own account and approve the Contractor's request for access.

Laboratory

The Laboratory is responsible for sample analysis and for providing the RP, Authorized RP Agent, or Contractor with data in EDF format, ready for GeoTracker upload and in some cases should provide the hard-copy of analytical reports..

In the vast majority of cases, RPs (and Authorized RP Agents) do not ask the Laboratories to upload their formatted EDF data files directly into the GeoTracker system. Typically, after performing an online error check, the Laboratory forwards the EDF files to the RP/Authorized RP Agent/Contractor, who reviews them to ensure the validity of the EDF data and then uploads the files to the State Water Board GeoTracker database.

In some cases, the RP (or Authorized RP Agent) may wish to have the Laboratory submit the EDF data directly to GeoTracker. In these instances, the Laboratory must first gain upload access to the site, in the same way that Contractors gain access: by logging onto the RP's GeoTracker account and requesting access to the site. The RP or Authorized RP Agent then logs onto his or her own account and approves the Laboratory's request for access.

Please note that GeoTracker Contractors *cannot* grant a Laboratory access to a site; only RPs and Authorized RP Agents can do so.

Regulatory Agencies

State Water Resources Control Board

The State Water Board is responsible for the overall operation and maintenance of the GeoTracker system and its successful use by all entities involved with soil and groundwater contamination issues. The State Water Board is also responsible for approving RP and Authorized RP Agent requests for upload access to facilities. Additional responsibilities of the State Water Board include: maintaining database security protocols; providing guidance and tools to standardize the review and quality of electronic compliance data submitted; and maintaining user accounts for RPs, consultants, and regulatory agencies.

Lead Regulatory Agency

The lead regulatory agency (whether the Regional Water Board, Local Oversight Program [LOP], or Local Implementing Agency [LIA]) receives electronic data, textual and graphical information submitted by the RP or consultant(s) for all unauthorized releases. This "receipt of data" includes reviewing the Field Point Names in the EDF (to verify whether names in the hard copy report match those in the electronic data) and noting whether the PDF of the hard-copy report has been uploaded to the GeoTracker regulator pages. Once the data have been "received," data are moved into the GeoTracker archive database and made available to the public.

State Water Board Resolution 2012-0016, adopted on May 1, 2012, directs regulatory agencies to review all cases in the petroleum UST Cleanup Program using the framework provided in the Low-Threat UST Case Closure Policy effective August 17, 2012. This review shall be accomplished within existing budgets and be performed no later than 365 days from the effective date of this policy. These case reviews shall, at a minimum, include the following for each UST case:

1) Determination of whether or not each UST case meets the criteria in this policy or is otherwise appropriate for closure, based on a site-specific analysis.
2) If the case does not satisfy the criteria in this policy or does not present a low threat based upon a site-specific analysis, impediments to closure shall be identified.
3) Each case review shall be made publicly available on the State Water Board's GeoTracker website in a format acceptable to the Executive Director.

The lead regulatory agency oversees the RP to ensure that current and accurate data are uploaded to GeoTracker. The accuracy, completeness, and timeliness of the data are critical because:

1) The data are used by the public to understand the conditions of sites;
2) The data are used by the real-estate industry to assess the value of sites and surrounding property;
3) The data are used by the federal, state, and local governments to make decisions related to priorities and funding; and
4) The data are used by the Office of Management and Budget, Congress, U.S. Environmental Protection Agency (USEPA) headquarters, and USEPA Region 9 to evaluate the effectiveness of the program.

Efficient use of GeoTracker by lead regulatory agencies can increase overall effectiveness in managing their caseloads. All incoming and outgoing compliance documents related to a LUFT site are included in GeoTracker, which makes them available to the public, other agencies, RP(s), and consultants and/or contractors who may work on the case. The regulators can effectively track incoming documents by their due dates and receive reminders when a document is past due. Used in this manner, GeoTracker assists in moving toward paperless case management.

Lead regulatory agencies are requested to ensure that all their open LUFT cases are properly claimed by RPs (or, alternatively, by their Authorized RP Agents) and that data for open cases are being submitted regularly. Additionally, lead agencies ensure that the proper case status for each site is correctly entered into GeoTracker and updated as the case status changes (e.g., assessment, remediation, closure).

Assistance with Use of GeoTracker

Help! Considerable documentation and guidance regarding GeoTracker are available at the State Water Board GeoTracker ESI web page: http://www.waterboards.ca.gov/ust/electronic_submittal/index.shtml

References

California Code of Regulations (CCR) Title 23 (Waters), Division 3. State Water Resources Control Board and Regional Water Quality Control Boards. Chapter 30. Electronic Submittal of Information.

California Code of Regulations (CCR) Title 27 (Environmental Protection), Division 3. Electronic Submittal of Information.

California State Water Resources Control Board (State Water Board), Resolution 2012-006, Low-Threat UST Case Closure Policy. Adopted May 1, 2012, effective August 17, 2012.

AB 2886 (Ch. 727, Stats. of 2000).

AB 358 (Ch. 571, Stats. of 2011).

Chapter 5: Health and Safety

September 2012

Scope of This Chapter

This chapter presents health and safety considerations for leaking underground fuel tank (LUFT) sites. It describes the need to incorporate worker and community health and safety into the LUFT cleanup process. This chapter is intended to provide a number of items to consider when preparing for and conducting field work at a LUFT site; however, the information in this chapter is not intended to be all-inclusive, as it is recognized that each organization has its own health and safety program and takes responsibility for the health and safety of the activities conducted by its employees.

Overview

Health and safety must be considered a priority in planning and implementing site activities. Recommended safety precautions, per Occupational Safety and Health Administration (OSHA) guidelines, can be used to protect associated parties and the environment and avoid both present and potential hazards. Actions should be documented as required by federal, state, and local regulations.

Safety Considerations

There are many worker and public health and safety issues to be considered during any activities conducted at a LUFT site. These issues include:

Transportation to and from the LUFT Site. It should be realized that there is the potential for a vehicular accident while driving to and from the site.

Mobilization and Demobilization. Traffic hazards should be considered when setting up the field support zone. It is recommended that workers wear high-visibility safety vests.

Personal Protective Equipment. It is important that workers at LUFT sites have the correct personal protective equipment (PPE).

Training. It is important that workers at LUFT sites have the proper training, including OSHA Hazardous Waste Operations and Emergency Response (HAZWOPER) training. More information regarding OSHA requirements is provided in the Worker Health and Safety Plan section below.

Dust. It is important to minimize potential exposure to dust generated as a result of the proposed activities. Control methods include covering sources, misting sources with water using stationary sprayers or water trucks, and halting activities altogether.

Noise. It is important to minimize the impact of noise to the workers onsite and occupants of neighboring properties. Make sure that occupational noise exposure standards and specifics regarding noise in 29 Code of Federal Regulations (CFR) 1910.120 Hazardous Waste Operations and Emergency Response (29 CFR 1910.120) are being met in the relevant Health and Safety Program. Note that noise ordinances are generally enforced from 7:00 p.m. to 7:00 a.m. on weekdays, depending on the jurisdiction and zoning. Weekend work is discouraged, and noise standards may be more stringent during the weekend. Nearby residents will appreciate any efforts to minimize noise generated by site activities.

Open Excavations. These are a risk to both workers and the public; secure fencing is recommended if excavations cannot be backfilled at the end of the work day. During excavation activities, the use of caution tape with delineators is recommended to avoid accidents near the excavated area. If workers need to enter the excavation area for any reason, shoring may be required; OSHA, state, and local regulations regarding shoring of excavations should be ascertained. Workers and onlookers who are not directly involved with the project must remain outside the enclosed area.

Buried Utilities. Underground utilities present a significant risk when excavation activities are planned at a LUFT site. It is important to provide proper notification to the local utility company. Areas with buried utilities can be located and marked by dialing 811 or 1-800-227-2600, *Call Before You Dig!*, a free, California utility-locating service. For confirmation, use of a private utility clearance company is also recommended.

Overhead Electrical Utilities. Overhead electrical utilities are a threat at a LUFT site when drill rigs, cranes, and excavators are used. If overhead electrical utilities are present, call the utility company and find out what voltage is on the utilities. Ask whether the utility company can shut off the utilities while work is taking place near them. If overhead utilities cannot be shut down, ask the utility company whether it can install insulation over the utilities during the time work will be taking place near them. Inform workers of overhead utility hazards and the precautions to prevent contact. Ensure that workers are not placed in dangerous proximity to high voltage by using a spotter, placing warning decals on equipment and drill rigs regarding the 10-foot minimum clearance, and conspicuously marking and maintaining marks of the location of overhead utilities. Consider overhead utilities energized (“hot,” “live”) until the local electric utility indicates otherwise.

Important! LOOK UP! BEST SAFETY PRACTICE: NEVER GET CLOSER THAN 10 FEET FROM AN OVERHEAD POWER LINE!

Heavy Equipment. Drilling and excavation equipment used and/or stored at LUFT sites is large and hazardous. Operator visibility may be marginal. Workers approaching, or working around, heavy equipment should exhibit extreme care and always be aware of their surroundings.

Stockpiled Soil. Stockpiled soil that has been staged for land farming or removal represents a potential hazard to the public and the environment if stockpiled soils are contaminated. This safety risk is best minimized by containing and covering stockpiles to prevent runoff and vapor or dust exposures, and by locating such stockpiles in a secured area of the site to prevent public exposure.

Vapors. Good site health and safety practices include minimizing public exposure to potential vapor emissions resulting from site activities and monitoring hazardous atmospheres for workers while they conduct activities at a LUFT site. Engineering and construction practices which typically reduce such emissions include the following: pumping out nonaqueous-phase liquids (NAPL); covering off-gassing excavations or stockpiles; backfilling off-gassing excavations with clean, non-impacted fill; using soils that have been stockpiled as backfill after receiving field confirmation (using field instrumentation) that the excavated soil is no longer off-gassing detectable vapors; misting excavations or stockpiles with water; covering excavations or stockpiles with foam or other vapor-suppressing agents; locating stockpiles away from and/or downwind of public receptors; and stopping work.

Explosion and Fire Hazard. The potential for explosion or fire hazards is of real concern at LUFT sites, due to the nature of working with petroleum products. It is important to properly monitor tanks, excavations, open areas, and enclosed spaces with a combustible gas indicator (CGI). An explosive environment is one containing 20% or greater of the Lower Explosive Limit (LEL). Spark and ignition sources should be avoided when an explosive environment is possible.

Stormwater. The consistent use of Best Management Practices (BMP) is intended to control surface runoff in order to prevent or minimize the transport of pollutants to receiving waters. Practices include, but are not limited to, the use of hay bales, hay socks, sand bags, and high-density polyethylene plastic to cover inlets. In some cases, a National Pollutant Discharge Elimination System (NPDES) permit may be required.

Investigation-Derived Waste (IDW). IDW is an additional hazard that may be present at LUFT sites. IDW can be different media, including (but not limited to) soil, water, and sludge. Refer to various guidance on management of IDW, such as the U.S. Environmental Protection Agency (USEPA) Guide to Management of Investigation-Derived Wastes (available online at http://www.epa.gov/superfund/policy/remedy/pdfs/93-45303fs-s.pdf).

Worker Health and Safety Plans

Legal.

Federal and State regulations require Health and Safety Plans (HASPs) for field activities where hazardous substances may be encountered. Language found in 29 CFR 1910.120 can be obtained from the U.S. Government Printing Office website:
http://edocket.access.gpo.gov/cfr_2008/julqtr/pdf/29cfr1910.120.pdf

OSHA requires a site-specific HASP for intrusive or other field-related work and requires that each HASP be appropriate for the proposed work. If the scope of work changes, a revised HASP may be required (to remain in compliance with OSHA regulations) before work is allowed to proceed.

Individuals working on or visiting a site in an official capacity must study the HASP before beginning any field activities. They must also familiarize themselves with the emergency telephone numbers within the HASP, any hazards which may be encountered, and the corresponding emergency response plan. A copy of the current version of the HASP must be available onsite during site activities. Each person involved in the work will attest, by signing the HASP, to the fact that he or she understands the hazards which may be involved, is familiar with the emergency procedures to be followed in case of an accident, and has the proper training for the tasks to be performed.

Site safety meetings to review the scope of the scheduled work, the pertinent safety concerns, and the relevant emergency procedures are held each day before work begins. Everyone who will participate in field activities that day attends this “tailgate meeting.”

The following are the minimum OSHA requirements for inclusion in an acceptable HASP:

- A list of the hazardous materials that may be encountered, and decontamination procedures and/or required emergency treatment for each material listed.
- A Material Safety Data Sheet (MSDS) should be available for hazardous materials used or stored onsite.
- An Activity Hazard Analysis (AHA), also known as a Job Safety Analysis (JSA), needs to be included for each activity that will be conducted at the site. This will include the potential hazards associated with each of the work activities.
- Name and job function (e.g., site geologist, driller, etc.) of the Site Safety Officer.
- Name and job function of the alternate Site Safety Officer.
- Name and job function of other responsible site personnel and their alternates.
- Addresses and phone numbers for the nearest emergency response facilities:
    - Fire Station
    - Ambulance Service
    - Police
    - Emergency Health Facility
    - Poison Control: 1-800-222-1222
- A map showing the most direct route to the nearest emergency health facility. This map must be at a scale that is easily read, and the route clearly identified, so that a person not familiar with the area can locate the facility with minimum delay. The map should be placed in a location that can be easily seen by workers, should an emergency be encountered.
- A narrative paragraph describing how to drive to the nearest emergency health facility, i.e., which roads, turns, and directions (left or right, and the approximate distance) are to be taken.
- Hazard Communication Plan: This includes addresses and telephone numbers for the responsible parties (RPs) and regulatory agencies to which accident reports must be provided, and the lines of communication for reporting a hazardous incident. The parties may include, but are not limited to:

- *Federal Government:* USEPA, OSHA, Centers for Disease Control (CDC), U.S. Coast Guard (USCG), etc.
- *State Government:* California Environmental Protection Agency (Cal/EPA), California Department of Toxic Substances Control (DTSC), Regional Water Quality Control Board (Regional Water Board), etc.
- *County/City Government:* Department of Environmental Health (or relevant county/city office), air pollution control district (APCD), etc.
- *RP and RP consultant(s).*

- Work-zone delineation, e.g., work zone, support zone, decontamination zone, restricted access zone, etc.
- Level of PPE required. If different work activities require different levels of protection, the requirements for each must be specified. For cases where Level A, B, or C is appropriate, workers must be trained in the use of the PPE required. No worker with facial hair which might prevent the tight fit of a respirator mask is to be assigned to tasks requiring Level A, B, or C PPE.
- Traffic control and site-access control procedures.
- Air monitoring procedures and safety limits.
- Procedures for managing weather-related problems, e.g., lightning, heavy rain, excessive heat, cold, wind, etc.
- Location of emergency equipment, such as fire extinguishers, vapor-suppressant applicators, etc. The individuals trained in and assigned to their use must be named and must be aware of their responsibilities.

Community Health and Safety Plans

Some regulatory agencies require that a Community HASP be included in the work plan in situations where public health and safety may be at risk. It is the responsibility of property owners, RPs, consultants, and subcontractors to conduct on-site activities in such a manner as to avoid the creation of any public health and safety hazards or nuisances. Precautions and continuing care to prevent impacts to the surrounding community are an ever-present concern, even in the absence of a Community HASP. If there will be significant noise or any risk to the community, at a minimum, a notice should be sent to community members who will be directly impacted.

References

29 CFR 1910.120, Hazardous Waste Operations and Emergency Response.

USEPA. 1992. Guide to Management of Investigation-Derived Wastes. January 15, 1992.

USEPA. 1992. Guide to Management of Investigation-Derived Wastes. April 1992. Available at http://www.epa.gov/superfund/policy/remedy/pdfs/93-45303fs-s.pdf

Chapter 6: Work Plans

September 2012

Scope of This Chapter

This chapter presents good practices for creating work plans used during the various phases of work at leaking underground fuel tank (LUFT) sites. Elements of various work plans and the work plan approval process are discussed.

Introduction

A work plan is a technical document that outlines both the scope of work (SOW) to be completed at a LUFT site and how the SOW is expected to be completed. The objective of the work plan should be clearly stated in scientific terms, not just to comply with a regulatory agency request. The work plan is also used to ensure that all parties involved clearly understand and agree on the SOW to be completed. A work plan provides a rationale for the proposed work, including sufficient information to allow the lead regulatory agency to evaluate the reasonableness of the proposed work. The work plan identifies the questions to be answered and how the proposed work/sample locations will answer those questions.

Work plans are written for a variety of activities (e.g., site assessment, over-excavation, well installation, well destruction, receptor surveys, etc.), and specific work plans are required for each type of event, depending on direction received from the lead regulatory agency.

Use of a CSM

The work plan should be developed to both address the regulatory agency's requests and to refine the conceptual site model (CSM). It is crucial that a CSM be used to determine data gaps and to make decisions regarding sampling at the site; the CSM should be updated as soon as new data are gathered, as discussed in the CSM chapter. The supporting data and analysis used to develop the CSM are not required to be contained in a single report and may be contained in multiple reports, including work plans, submitted to the regulatory agency over a period of time. It should be noted that, if an RP wishes to close a case under the State Water Resources Control Board (State Water Board) Resolution 2012-0016 adopted May 1, 2012, Low-Threat Underground Storage Tank Case Closure Policy (Case Closure Policy) effective August 17, 2012, a CSM must be developed.

Note: The cost and burden of requests for work plans or further work should bear a reasonable relationship to the need for such reports and the benefits to be obtained from the reports (see State Water Board Resolution 1992-0049, section III.B). If the case is regulated by the Regional Water Quality Control Board (Regional Water Board) and the responsible party (RP) feels the request for work is not reasonable, or if there is a failure to act by the Regional Water Board, the RP may be able to file a petition for review with the State Water Board (see California Water Code [WC] Section 13320). However, it is highly recommended that the RP try to resolve the issue with the Regional Water Board and that a petition be a last effort.

Legal.

The California Code of Regulations (CCR) Title 23, Division 3, Chapter 16, §2722, "Scope of Corrective Action," requires that a work plan be submitted to the regulatory agency for review and comment prior to implementing any phase of investigation or corrective action associated with regulated underground storage tank (UST) systems. These laws require work plans for the following activities:

- Post-tank-removal corrective actions
- Interim remedial actions
- Preliminary site assessments
- Soil and groundwater investigations
- Corrective action plans
- Verification monitoring programs

Work Plan Approval Process

When a lead regulatory agency requests that an RP undertake an action at a LUFT site, it is the responsibility of the RP to prepare a work plan that provides the details of the activities to be implemented. This Manual recommends that the work plan include a schedule and timeline, be signed by the appropriate licensed professional, and be submitted within the time allotted. In most cases, the RP's authorized agent/consultant will prepare the work plan on behalf of the RP. The work plan is to be submitted to the lead regulatory agency for review.

- **Once agency concurrence is received**, work can begin and progress as scheduled unless the deadline will not be met, in which case the RP needs to request written permission for an extension and provide justification for the extension as soon as it becomes apparent the deadline will not be met. The RP shall modify the work plan, as necessary, at the direction of the regulatory agency and resubmit it to the regulatory agency for concurrence. After work is complete, the RP submits a report stating that the work is complete.

The RP may begin implementation of the work plan 60 calendar days after submittal, unless the RP is otherwise directed in writing by the regulatory agency. Before beginning these activities, the RP must:

- **Notify the regulatory agency** of the intent to initiate the actions proposed in the submitted work plan.
- **Comply** with any reasonable, appropriate, and technically justified conditions set by the regulatory agency, including mitigation of adverse consequences from the cleanup activities.

Important! Even though an RP may begin work 60 days after a work plan has been submitted, regardless of whether the agency has issued concurrence, site work conducted without appropriate authorization may not be accepted by either the regulatory agency (e.g., the work is not technically defensible) or the UST Cleanup Fund (e.g., the work was not justified, or was not conducted in the most cost-efficient manner).

Chapter 6: Work Plans
Work Plans for Site Assessment

September 2012

Site Assessment Work Plans

There are two types of work plans used during site assessment: **fixed** and **dynamic**. Each type should be used in development of the CSM.

When a **fixed work plan** is utilized, the consultant/RP determines exactly where sampling will occur, how many samples will be collected, and the duration of the investigation. This is referred to as a “multiple-phase approach” to site assessment. The benefit of this type of work plan is that the stakeholders know the cost of the project and exactly which tasks will be conducted (with the exception of slight field variances). The drawback to this type of work plan is that, as the field sampling occurs, new issues may arise, but the consultant/RP cannot collect further samples because the sampling activities have not been approved by the regulator in a work plan.

When a **dynamic work plan** (referred to as the “the Triad Approach” by the United States Environmental Protection Agency (USEPA) is utilized, all stakeholders agree to certain field sampling procedures and general sampling locations, but modify the sampling based on field conditions. This is referred to as a “single-phase approach” to site assessment. Because of the dynamic nature of this type of work plan, the overall process can be expedited, but the exact cost of the investigation is unknown prior to heading into the field.

Important! The expedited site assessment (ESA) process is a framework for rapidly characterizing UST site conditions for corrective action decisions (USEPA 1997). This concept has been described by other names, including: accelerated site characterization, rapid site characterization, and expedited site investigation.

More information on the ESA process and how to develop a work plan can be found in the *Expedited Site Assessment Tools for USTs: A Guide for Regulators*, at the following website: http://www.epa.gov/oust/pubs/sam.htm

Elements of a Fixed Work Plan

The following elements should be considered when developing a fixed work plan. Each work plan will vary, based on the necessary activities, and should be specific to site conditions. The level of effort and details in a particular work plan are determined by the responsible professional in charge of the investigation, with input from regulatory agencies as appropriate.

Proposed Work and Technical Approach

The proposed work needs to include details such as proposed sample locations, number of samples, analyte list for samples, field quality control (QC) samples, laboratory QC samples, and justification for the proposed work in sufficient detail to allow the regulatory agency to evaluate the rationale of the proposed work and conformance with minimum locally accepted professional practices and standards; and will consider the criteria of the Case Closure Policy when applicable.

The work plan describes anticipated methodologies and procedures. This Manual recommends that Standard Operating Procedures (SOPs) be included as an appendix to the work plan. If there are any planned deviations from accepted practices, this Manual recommends that reasons for their selection be provided. Methodologies and procedures for work plans include, but are not limited to:

- Underground utility locating,
- Drilling,
- Well construction and development (if monitoring wells are, will be, or are expected to be installed),
- Sampling, and

- Decontamination of sampling tools.

The work plan indicates how the analytical results will be evaluated and provides an estimated timeline for completion of the work.

Assumptions

This discussion in the work plan includes identifying and justifying any and all assumptions made in the work plan.

Analytes and Methods

The target analytes and analytical methods to be used at a LUFT site are described in the Laboratory Analysis and Methods chapter of this Manual.

Reporting Requirements

This section describes the anticipated reporting procedures for the findings from the work to be conducted. Reports are discussed in more detail in the Reports chapter of this Manual.

Performance Measures

It is important for the consultant performing the work at the site to document site activities. This discussion in the work plan should clarify how the proposed work will move the site toward closure and how performance will be monitored and documented.

Elements of a Dynamic Work Plan

The majority of the information presented in this section was extracted from “USEPA Guidelines for Dynamic Work Plans” (USEPA 2001). The dynamic work plan is not as commonly used as the fixed work plan, generally because there can be uncertainty associated with the cost and scope of the project (see the Pros and Cons of Dynamic Work Plans section below). .

Elements to consider for incorporation into dynamic work plans include:

Systematic Planning

Create clearly stated goals and objectives, and define scientifically and legally defensible site decisions using a well-rounded technical team and stakeholder input. This includes plans to fulfill the criteria required in the Case Closure Policy (see the Risk Evaluation and Risk Management chapter for the criteria in this policy). Extensive planning is performed to help the field team prepare for the challenges that may arise during site assessment and to ensure that the team will not be thwarted by obstacles that arise during the site visit. It is important for all stakeholders to be in agreement on the approach prior to the commencement of site activities.

On-Site Generation of Data

Real-time analytical methodology is used to provide qualitative and semi-quantitative data. When data are generated immediately, site decisions can be made efficiently and the sampling strategy can be adjusted according to the new data.

High-quality quantitative data can be obtained from a wide variety of rugged field analytical equipment and from mobile laboratories. Any mobile laboratories used in California are required to be certified by the Environmental Laboratory Accreditation Program (ELAP).

Immediate Decision-Making Capability

The on-site generation of data helps define hot spots and can assist in determining whether the removal or treatment of contaminated media is preferable, while minimizing the collection and analysis of uninformative samples as well as determining risk to human health and the environment.

Adaptive Sampling and Analysis Strategy

As data results are either generated or received, a strategy for making decisions must already be in place. Also, as sampling data are obtained, the established CSM is evaluated for accuracy. It is extremely important that goals and objectives be clearly defined, because the constant flow of decisions that need to be made will be based on the goals and objectives of the work.

For additional information, see the USEPA guidelines at http://www.epa.gov/tio/download/char/dynwkpln.pdf .

Pros and Cons of Dynamic Work Plans

Advantages of dynamic work plans include:

- Site assessment can be accomplished more rapidly.
- The cost of field work is often reduced because the process is condensed.
- The number of borings may be reduced because real-time feedback of analytical results facilitates more appropriate location of subsequent samples.
- The cost of preparing documents is reduced because only one (or possibly two) work plan(s) and assessment report(s) is(are) necessary.
- The assessment process has less impact on the environment (i.e., it is a greener process) because of the reduced number of mobilizations.
- Remediation of the site can commence sooner, so that constituents of concern (COCs) may not have spread as far from the source, which will limit the area to be remediated.

Disadvantages of dynamic work plans include:

- It may be difficult to estimate the cost of the sampling effort.
- Field sampling equipment may be less precise than fixed-laboratory analysis.
- The RP and consultant(s) may be reluctant to choose this strategy because the cost and scope of the project are undefined. That is, more or less sampling may be required than originally thought.

References

California Code of Regulations (CCR) Title 23 (Waters), Division 3. State Water Resources Control Board and Regional Water Quality Control Boards. Chapter 16. Underground Tank Regulations Article 11. Corrective Action Requirements §2722.

California Water Code (WC), Section 13320.

California State Water Resources Control Board (State Water Board), 1992-0049, amended October 2, 1996.

State Water Board, Resolution 2012-006, Low-Threat UST Case Closure Policy. Adopted May 1, 2012, effective August 17, 2012.

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Chapter 7: Corrective Action Plan

September 2012

Scope of This Chapter

This chapter presents good practices for creating a Corrective Action Plan (CAP) to be used during mitigation measures. Elements of a CAP include an assessment of the impacts, a feasibility study, and applicable cleanup levels and goals. A CAP may include goals to satisfy criteria under the Low-Threat Underground Storage Tank Case Closure Policy (Case Closure Policy) (see criteria in the Risk Evaluation and Risk Management chapter).

Some possible objectives of a CAP are to:

- Provide a Conceptual Site Model (CSM) to support the proposed corrective action, as required to meet the general criteria of the Case Closure Policy, and is not required to be contained in a single report;
- Provide a feasibility study explaining how and why the proposed corrective action is practicable, appropriate, and cost effective;
- Identify the limitations of the corrective action;
- Provide a conceptual design of the corrective action and a description of the tasks necessary to implement the corrective action;
- Provide detailed design plans, schedule, and specifications, including an operation and maintenance (O&M) manual for the corrective-action system and emergency contingency plans in the event of any significant failure of the corrective-action system;
- Identify the necessary easements and permits required to implement the corrective action;
- Set the remedial action schedule and objectives;
- Provide a plan for performance evaluation during the entire life cycle of the remediation system; in other words, parameters to be reported and planned reporting frequencies to monitor the effectiveness of the corrective action and to describe incremental reductions of contaminants in soil and groundwater;
- Identify the residual contaminant concentrations in soil and groundwater that meet the criteria of the Case Closure Policy; and
- Establish criteria for ending corrective action.

CAP Preparation

Preparation of a CAP is predicated on the basis that the site assessment and CSM are complete to the point that initiating remediation will be feasible based on site conditions. Some forms of remediation can be implemented without full delineation and still attain remediation goals (see Rapid Response/Interim Remediation section in the Release Response Prioritization chapter).

Legal.

As defined in the Underground Storage Tank (UST) Regulations, *California Code of Regulations* (CCR) Title 23, Division 3, Chapter 16, Article 11, §2725, the responsible party (RP) shall propose a CAP based on the information obtained during the site investigation and with concurrence from the lead regulatory agency. The CAP shall include an assessment of the impacts, a feasibility study, and applicable cleanup levels.

UST Regulations, CCR Title 23, Division 3, Chapter 16, §2722 (c) states that the RP shall submit the CAP to the regulatory agency for review and concurrence, and shall modify the CAP in response to a final regulatory agency directive.

The RP must notify all impacted parties of the proposed CAP (Health and Safety Code [H&SC] §25297.15). The public will also need to be updated on the corrective actions proposed (see Public Participation in the Roles and Responsibilities chapter).

CAP Implementation

The responsibility for implementing the CAP lies with the RP. The RP shall monitor, evaluate, and report the results of the implementation of the CAP on a schedule agreed to by the lead regulatory agency. Annually, or at the request of the RP or party conducting the corrective action, the lead regulatory agency shall conduct a review to determine whether the site meets the Case Closure Policy criteria. The RP shall maintain the corrective action until the applicable goals have been met.

Important! During implementation and progression of the CAP, remember to re-evaluate and update the CSM to incorporate new data and any new understanding(s) of site conditions.

A RP may begin cleanup of soil and water before regulatory concurrence if the lead regulatory agency has not provided a response within 60 calendar days of CAP submittal. In this situation, the RP must still notify the regulatory agency of his/her intention to begin cleanup and to comply with any conditions set by the regulatory agency, and shall modify or suspend activities when directed to do so by the regulatory agency. It is recommended that regulatory approval be received prior to beginning work, as this may assist with the overall cost-effectiveness of the corrective action.

Legal.

According to CCR Title 23, Division 3, Chapter 16, UST Regulations, Article 11 §2726, the RP shall monitor, evaluate, and report the results of implementation of the CAP on a schedule agreed to by the lead regulatory agency.

The UST Cleanup Fund Regulations, CCR, Title 23, Division 3, Chapter 18, Article 4 §2811(a)(5) specify that, for a case that has been accepted into the UST Cleanup Fund, corrective-action costs incurred after December 2, 1991, are reimbursable only if the work is completed in compliance with applicable corrective action requirements "including the implementing regulations in CCR, Title 23, Division 3, Chapter 16, Article 11." The requirement to prepare a CAP before initiating corrective action is described in Article 11. The regulations in Article 11 are explicit about the minimum requirements for a CAP. Different regulatory agencies may have additional requirements, or clarifications, on what they expect a CAP to include.

Example CAP Contents

The lead regulatory agency must be consulted to determine its requirements for the organization and submittal of the CAP. Some agencies require the CAP to be submitted in the form of separate documents, e.g., a Feasibility Study and a Remedial Action Plan. Additionally, some agencies refer to the Feasibility Study as a "CAP" and will require a subsequent Remedial Action Plan to complete the CAP requirements. The following items are points to be considered when preparing a single CAP document:

Introduction

Introductions should include the purpose of the corrective action and the site description, including geologic and hydrogeologic information.

Summary of Previous Work

The goal of this section is to describe the previous site work, identify the major conclusions of each phase of work, and reference the reports containing the details. This section does not necessarily require a restatement of all the details of each past report or laboratory results for each sample. The primary objective of this section is to include relevant prior data in context with the goals of the CAP. This section may include work performed to date to assess and mitigate the release, evaluation of risk, and feasibility of cleanup methods.

Justification of Cleanup Goals

This section of the CAP should discuss the cleanup goals that the lead regulatory agency, RP, and consultant determine to be appropriate and achievable. Additionally, the lead regulatory agency, RP, and consultant should evaluate criteria required for closure under the Case Closure Policy. Cases that meet the general and media-specific criteria described in this policy pose a low threat to human health and safety or the environment, and are appropriate for closure pursuant to H&SC §25296.10. Additionally, State Water Board Resolution 1992-0049 is a state policy for water quality control and applies to fuel UST cases. This resolution directs that water affected by an unauthorized release attain either background water quality or the best water quality that is reasonable if background water quality cannot be restored. Any alternative level of water quality less stringent than background must be consistent with the maximum benefit to the people of the state, not unreasonably affect current and anticipated beneficial use of affected water, and not result in water quality less than prescribed in the water quality control plan for the basin within which the site is located. The resolution does not require, however, that the requisite level of water quality be met at the time of case closure. It specifies compliance with the cleanup goals and objectives within a reasonable timeframe.

If there are future development, land-use changes, and/or beneficial use changes, the site risk and potential future receptors may need to be re-evaluated. Collaboration with the lead regulatory agency is suggested to determine how to incorporate potential future risk into the CAP.

See the Risk Evaluation and Risk Management chapter for more information regarding the process of evaluating and managing risk at a leaking underground fuel tank (LUFT) site, including a detailed discussion of the Case Closure Policy criteria should the site qualify following remediation activities.

Legal.

According to UST Regulations, CCR Title 23, Division 3, Chapter 16, Article 11 §2725, "for waters with current or potential beneficial uses for which numerical objectives have been designated in water quality control plans, the [RP] shall propose at least two alternatives to achieve these numerical objectives. For waters with current or potential beneficial uses for which no numerical objectives have been designated in water quality control plans, the [RP] shall recommend target cleanup levels for long-term corrective actions to the regulatory agency for concurrence. Target cleanup levels shall be based on the impact assessment."

Corrective Action Selection

When evaluating potential corrective actions, it is important to compare different technologies to determine which method is the best for site conditions and achieves either cleanup goals or compliance with Case Closure Policy criteria in a reasonable time period with reasonable costs. It is prudent to compare at least three technologies. If these goals cannot be achieved, it may be appropriate to demonstrate the technical infeasibility of implementing cleanup and look to other available methods to mitigate human or environmental risk at the site.

- Include results and data obtained from any treatability or pilot study. These data are the basis for the remedial design and demonstrate the effectiveness of the proposed remediation system(s). Data analysis includes evaluation of suitable corrective actions and the residual contaminant concentration associated with each evaluated corrective action.
- Provide the anticipated amount of time to achieve the proposed cleanup goals for each proposed corrective action.
- Provide a cost comparison of the various methods. Cost analyses include all aspects of the proposed corrective action (e.g., planning, construction, operation, maintenance, reporting, verification monitoring, disposal, and decommissioning).

Recommended Corrective Action

This section describes how the best available, most cost-effective remedy is expected to reduce subsurface concentrations of constituents of concern (COCs) to cleanup goals or Case Closure Policy criteria. Supporting evidence is needed to justify a high level of confidence that the goals will be met.

System design and plans of the recommended corrective action should include:

- A description of the remediation process and an overview of the equipment required. Remediation design elements may include construction plans (electrical one-line drawings, construction drawings in plan view and/or details, piping or wellhead construction details, remedial well design detail, shoring/grading plans), and other engineering documents.
- A description of the expected pumping rates, treatment efficiencies, etc.
- Certification of the plans by an appropriate registered professional (e.g., a professional certified electrical engineer prepares or stamps electrical one-line drawings).

Endpoint for Remediation

This section describes the criteria for remediation completion and site closure. It includes a description of how remediation system performance will be documented, and how the progress of the remediation process is monitored. The CAP needs to discuss contingency measures for addressing residual plume components if the proposed method is unsuccessful in meeting the remediation goals. If there are future development, land-use changes, and/or beneficial use changes, the site and potential future receptors may need to be re-evaluated. Collaboration with the lead agency regarding inclusion of this into the CAP is suggested. The Remedial Effectiveness section in the Remediation chapter provides parameters and considerations for determining the effectiveness of a corrective action.

Part of preparing a CAP is identifying the life-cycle expectations for the remediation process, including appropriate means of documenting progress and criteria for the remediation endpoint. It is wise for regulators, RPs, and consultants to agree on the conditions under which the operation of the remediation system will be stopped before initiating active remediation.

Additional Implementation Details

The following data may be included in the CAP or as part of a subsequent document, as required by the lead regulatory agency:

Remediation Equipment, Specifications, and/or Materials

This section includes a brief description of equipment specifications or materials to be used during remediation. Appendices may include:

- Manufacturer specification sheets
- Detailed engineering calculations (flow rates, pipe sizes, discrete vapor samples, water table draw-down, effective radius of influence, etc.)
- Copies of design drawings
- Process flow charts
- Permits
- Dedicated well head equipment
- Logic control settings (pulse extraction events)

Waste and/or Materials Management

This section describes any waste or materials-handling requirements associated with the remediation process; for example, management of:

- Granular activated carbon
- Extracted groundwater
- Excavated soil
- Used oil from remediation equipment
- Construction debris from remediation system installation
- Soil cuttings from remediation wells

- Hydrogen peroxide used for advanced oxidation
- Nutrients for bioremediation

Wells or Other Subsurface Features

This section describes the number and placement of remediation wells necessary for an effective cleanup process or, if a remediation trench is to be installed, a description of its construction and placement.

Permits and Schedule for Implementation

Permit Examples

- **Air:** Air Pollution Control District (APCD) Permits (Permit or Authority to Construct or Permit to Operate, or other). Generally, any type of air discharge requires a permit.
- **Water:** Publicly Owned Treatment Works (POTW) (Sewer Discharge) (City or County) or National Pollutant Discharge and Elimination System (NPDES) Permit (Storm Drain Discharge) (Regional Water Quality Control Board).
- **Waste Discharge** (required by some Regional Water Quality Control Boards for injection processes).
- **Well Permits** (obtain from the Public Works Agency, local City or County well ordinance or equivalent): Groundwater well permits and groundwater well abandonment permits, boring permits
- **City or County Building, Electrical, Encroachment, Planning, Noise, or Fire Department Permits**
- **Shoring/Grading Permits**
- **Access agreement**

Schedule

A schedule should be included with the CAP. The following milestones are examples of points to consider when developing the schedule:

- CAP concurrence by agency.
- Remediation design/plan completion.
- Any required Access Agreements for private property.
- Emissions or discharge permits.
- Construction bid/procurement (consultants or specialty construction contractors, including drillers).
- Building/construction permits.
- Any required well or drilling permits.
- Construction of remedial technology onsite.
- Startup and shakedown and/or baseline sampling. Schedule for submitting results of start-up sampling.
- Transition to routine O&M. At this stage, the site transitions from the startup phase to routine operations. Schedule for submitting sampling data prior to system status reports.
- Estimated time to verify completion of project, remove system, prepare a No Further Action (NFA) Request, and for the lead regulatory agency to issue an NFA letter.

> **Note.** The lead regulatory agency will be able to provide agency-specific requirements for the schedule as well as any other additional requirements for the CAP.

References

California Code of Regulations (CCR) Title 23 (Waters), Division 3. State Water Resources Control Board and Regional Water Quality Control Boards. Chapter 16. Underground Tank Regulations Article 11. Corrective Action Requirements §2722.

California Health & Safety Code (H&SC), Section 25295.

California Water Code, Section 13320.

U.S. Environmental Protection Agency (EPA). 1997. Expedited Site Assessment Tools for Underground Storage Tank Sites - A Guide for Regulators. Available at http://www.epa.gov/oust/pubs/esa-ch2.pdf. Accessed on 24 March 2011.

EPA. 2001. A Guideline for Dynamic Workplans and Field Analytics. Available at http://www.epa.gov/swertio1/download/char/dynwkpln.pdf . Accessed on 24 February 2010.

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State Water Board, Resolution 2012-006, Low-Threat UST Case Closure Policy. Adopted May 1, 2012, effective August 17, 2012.

Chapter 8: Reports

September 2012

Scope of This Chapter

This chapter discusses some of the reports needed during the various phases of work at leaking underground fuel tank (LUFT) sites. The specific reports described in this chapter are Underground Storage Tank (UST) Removal Reports, Site Assessment Reports, Monitoring Reports, and Case Closure Requests.

Many different reports are required to present the results of work performed at LUFT sites. These scientific documents are used to determine the direction of the project and to provide verification of the various phases of investigation, assessment, remediation, monitoring, and closure. Reports are used to present information to stakeholders regarding the status of the various phases of work conducted at LUFT sites. The main elements of a technical report are data, data analysis, conclusions, and recommendations.

Reporting Schedule

Technical reports are to be submitted to the regulatory agency case worker by the assigned due date, as required by the regulatory agency (*California Code of Regulations* [CCR] Title 23, 2652d). If the report cannot be submitted by the assigned due date, the responsible party (RP) or consultant may submit a written request for extension, citing the specific reason for the extension request and an anticipated date by which the report can be submitted. It is the RP’s responsibility to provide acceptable justification for an appropriate proposed extension.

Concurrence with Reports

The agency case worker reviews reports to determine whether the activities associated with various phases of work at a LUFT site have been conducted and completed as set forth in the respective work plan. The agency is to consider the conclusions and recommendations presented in the report and determine whether further work is required. Based on the agency’s assessment, the case worker will provide direction to the RP/RP’s consultant on how to proceed.

GeoTracker Reporting Requirements

All reports need to be uploaded to GeoTracker, an on-line tool for submitting data and reports electronically within the State of California, as discussed in the GeoTracker chapter of this Manual.

Chapter 8: Reports
Specific Report Types

September 2012

This section provides some examples of specific report types that may be required for work performed at a LUFT site. This is not intended to be a complete list of the applicable reports, nor is it intended to list every detail that may be required for each report. It is important that the RP/consultant work with the regulatory agency overseeing the case to agree on the expectations for reports and level of detail for the various phases of work at a LUFT site. Additionally, it is important to understand agency expectations regarding whether the various reports need to be signed by a California licensed professional geologist or engineer. It is the responsibility of the RP to check with the respective lead agency for its specific requirements.

UST Removal Reports

A UST Removal Report is generated when a UST is permanently removed from its existing location. The process of removing a tank is discussed in the Tank Removal and Closure in Place chapter of this Manual. The report customarily includes the following sections:

Signature Page

Some agencies may require supervision of UST removal by a California-licensed professional geologist or engineer. The registered professional may need to sign off on the provided UST Removal Report. It is the responsibility of the RP to check with the respective lead agency for its specific requirements.

Introduction

Background information is provided in the UST Removal Report, including the site description, locations of the UST and appurtenances, type and size of UST, and original date of tank installation. Figures show site location and locations of tank(s) and appurtenances.

Description of Removal Activities

- **Permits:** There are different permit requirements depending on the location of the site and the associated agency jurisdiction. This section of the report sets forth how the RP and/or the consultant have complied with the permit requirements.
- **UST Content Removal and Cleaning:** Describes the procedures employed for cleaning the UST, the quantity of wastewater, and disposal manifest.
- **Excavation:** Includes the dimensions of the excavations required to remove UST and appurtenances, the condition of soil (odor, staining, visual inspection), and description of the type of soil. Accounts for sampling and tracking of uncontaminated and contaminated soil stockpile(s) to determine re-usability, if any. It also provides information on over-excavation for areas with contaminated soil and disposal manifests (as applicable).
- **UST and Appurtenance Removal:** Includes the date of removal and description of how the tank was rendered inert; also includes oxygen, carbon dioxide, and lower explosive limit (LEL) readings collected in the tank, the excavation, and the breathing zone. This discussion may also include a description of the tank condition upon removal, location of tank disposal, and a disposal manifest. It is desirable to map the known locations of UST and appurtenance releases, if possible.
- **Confirmation Sampling:** Describes where the soil and groundwater (if standing water was encountered in the excavation) samples were collected, the sampling and handling procedures, and summarizes the analytical results. See the Tank Removal and Closure in Place chapter for the definition and strategies for confirmation sampling.
- **Backfill:** This section reports whether the excavated soil is useable for backfill, and includes the analytical results for soil samples to support either a positive or negative verdict on the soil's usability. If "new" fill material is needed, the source and type of soil, as well as the analytical data on the fill, are

included. The procedure for backfilling is discussed, and compaction testing is also included. **Note:** It is highly recommended that regulatory concurrence be obtained to backfill with excavated soil from the tank pit.

Conclusions

This section summarizes the activities performed during the UST removal. It also indicates whether further assessment and remediation activities are recommended based on the analytical results obtained during the removal, tank structural failure, and/or other visual observations during the tank-removal process, or whether the tank meets tank-closure criteria. If the UST is determined to be leaking, an Unauthorized Release Report (Health and Safety Code [H&SC] 25295 (a)(1)) will be submitted by the RP or consultant, and a LUFT case opened up by the regulator within GeoTracker.

Site Assessment Reports

A Site Assessment Report is prepared to report on the investigative activities performed at and analytical data gathered from a LUFT site. The following items may be included in Site Assessment Reports:

Signature Page

A California licensed professional geologist or engineer may need to sign off on the Site Assessment Report. It is the responsibility of the RP to check with the respective lead agency for its specific requirements.

Presentation of Historical and Recent Site Data

- Site plan with locations of all borings, wells, and other sampling points.
- If previous site assessment data exist, include maps and cross-section(s) showing the soil and bedrock characteristics, and the distribution of contaminants, in both soil and groundwater.
- Table(s) of soil analytical results (in milligrams per kilogram [mg/kg], with both recent and historical data in chronological order.
- Table(s) of groundwater analytical results (in micrograms per liter [µg/L], with both recent and historical data in chronological order and tabulated by well number.
- Maps and/or cross-sections of soil and groundwater analytical results for different analytes. Estimated plume maps may be drawn to illustrate where data are extant and where there may be a lack of data.
- Boring logs and well logs of the most recent site-assessment work. Description of the site-specific geology and hydrogeology, updated with the most recent investigative results. See Site Assessment chapter.
- Revision(s) to the Conceptual Site Model (CSM), which resulted from the current phase of work, are presented and discussed in the report text.

Description of Site Assessment Activities

- Investigative procedures used, including soil, groundwater, and/or vapor sampling.
- Description of locations and the number of all borings, wells, and other sampling points.
- Description of groundwater-well installation as applicable. Guidelines for monitoring well design and construction for hydrogeologic characterization can be found at: http://www.dtsc.ca.gov/SiteCleanup/upload/SMP_Monitoring_Well_Design.pdf.
- Analytical methods used.
- Changes, if any, to the scope of work, and rationale for any such changes.
- Decontamination procedures.
- Waste management (including stockpiles) and disposal procedures.
- Storm water pollution prevention procedures.

Interpretation of Data

It is necessary to interpret the analytical and visual data collected during the investigation to identify source and release areas, delineate the extent of contamination, and establish plans for mitigation. This is accomplished by comparing the data results to the criteria established in State Water Resources Control Board (State Water Board) Resolution 2012-0016 adopted May 1, 2012, Low-Threat UST Case Closure Policy (Case Closure Policy) effective August 17, 2012, when applicable. For sites that do not meet the parameters of the Case Closure Policy, a site-specific risk assessment may be recommended (see the chapter on Risk Evaluation and Risk Management for more details).

The interpretation of data generally includes a statement about data validation, conformance with quality assurance / quality control (QA/QC) limits or data quality objectives (DQOs), acceptable reporting limits, etc. If DQOs have not been met, a statement is provided regarding whether the data are still valid and useable, and the underlying rationale for the conclusion. This section of the Site Assessment Report may also include an assessment of residual concentrations for constituents of concern (COCs) in soil and/or groundwater.

Conclusions and Recommendations

The technical report presents pertinent conclusions based on the interpretation and analysis of site-specific data by the RP or its consultant. The technical report also proposes recommendations for the next phase of work at the site or, if appropriate, presents a request for case closure if the criteria established in State Water Board Resolution 2012-0016, the Case Closure Policy, have been satisfied or a risk assessment has indicated that the site poses no significant risk to human health, safety, or the environment (see Risk Evaluation and Management chapter and Case Closure Request section below).

All conclusions should be *supported*, not merely listed. This section should also:

- Discuss whether the work satisfied the work-plan objective(s);
- Indicate which case-closure criteria were satisfied; and
- Indicate which (if any) significant data gaps remain to satisfy case-closure criteria.

Monitoring Reports

Periodic monitoring at LUFT sites may be needed; for example, to monitor the stability of a groundwater plume and/or ascertain the performance of the remedial system(s) installed. A report is submitted to the regulatory agency in a timely fashion after each monitoring event. For a remedial system(s), the monitoring report includes information on system status and operation, monitoring records, and an evaluation of progress for targeted areas, including volumes treated, and amount of hydrocarbons removed. Any changes, modifications, or other significant information which may affect the remedial design modifications are also reported. The frequency of monitoring and reporting intervals may change, based on direction from the lead regulatory agency. It is important that licensed professionals review and sign reports that contain an accurate interpretation of the groundwater monitoring, sampling, and laboratory data; conclusions about the data; and recommendations for future corrective action.

Legal.

Per State Water Board Resolution 2009-0042, quarterly groundwater monitoring was reduced to semi-annual or less frequent monitoring at LUFT sites. However, the initial reporting frequency as established in the Corrective Action Plan, which could be quarterly or even monthly, may change over time, and be reduced to semi-annual or even annual reporting at some point later in the assessment process. If more than semi-annual monitoring is required for a case, the RP and State Water Board shall be notified of the rationale by the lead regulatory agency, and the notice posted on GeoTracker.

Case Closure Request

When the RP has performed corrective actions (including assessment, remediation, and/or monitoring, as applicable) required by the lead regulatory agency to ensure that the site meets the criteria of the Case Closure

Policy and/or poses no significant risk to human health and/or the environment, as proven in a site-specific risk assessment, the RP or its consultant prepares a technical report justifying the request for case closure. It is also the responsibility of the RP to notify all impacted parties of the proposed closure (California Health & Safety Code [H&SC] 25297.15).

Effectiveness of Remedial Actions

This section identifies cleanup levels, the areas and media targeted by the remediation, the type of remediation used, the period of time over which various remedial options have been implemented, and the effectiveness of the remedial action(s) in reducing the concentrations of COCs and meeting remedial objectives. System operation and maintenance (O&M) data, and monitoring and verification sampling data are presented to substantiate the conclusions presented in this section.

Summary of Case Closure Request Elements

Completeness in closure reporting helps the closure process proceed more efficiently, so it is recommended that the lead agency be contacted for its closure reporting requirements. The following are elements that may be included in the Case Closure Request:

- Site history and background information pertinent to closure concerns;
- Identification of receptors within ½ mile of the site, including a vicinity map clearly identifying the site, the receptors, and surrounding land use;
- Service area of public water system;
- Distance to nearby surface water and water supply wells;
- Identification of current and future land use at the site and surrounding properties;
- Cumulative tables with groundwater information (analytical results and depth to groundwater), discussions regarding trends in current and historic groundwater conditions, and historic groundwater flow directions plotted on a site map;
- Cumulative tables with all soil sampling results;
- Tables showing the maximum soil and groundwater concentrations detected at the site, as well as tables showing the highest soil and groundwater concentration levels and deepest soil and groundwater concentrations remaining at the site after remediation;
- Site maps showing maximum detected groundwater concentrations and current groundwater conditions in each well;
- Site maps and cross-section(s) showing lithology, boring and well locations and depths, sampling results, contaminant contours, and remediation locations;
- Tables and graphs showing vapor concentrations as well as periodic and cumulative vapor hydrocarbon removal rates and volumes, if vapor extraction has been conducted at the site;
- Tables and graphs showing periodic and cumulative free product and groundwater removal rates and volumes, if free product and/or groundwater remediation has been conducted at the site;
- Calculated mass remaining *in situ* and contaminant degradation rate;
- Disposal information concerning any impacted materials generated at the site, such as manifests (when available); and
- All current record owners of fee title to the site must be identified and notified of the closure request – this documentation must be included in the Case Closure Request to confirm that this task has been completed.

References

State of California State and Consumer Services Agency. 1998. The California Board of Geologists and Geophysicists. Guidelines for Groundwater Investigation Reports. http://www.sawpa.org/documents/roundtable/Salinity/groundwater_guidelines.pdf. July.

California State Water Resources Control Board (State Water Board), Resolution 2012-006, Low-Threat UST Case Closure Policy. Adopted May 1, 2012, effective August 17, 2012.

Chapter 9: Green and Environmentally Responsible Cleanups

September 2012

Scope of This Chapter

The use of environmentally responsible, or “green,” strategies to remediate contaminated Leaking Underground Fuel Tank (LUFT) sites is encouraged. Although cleanup improves the local environment at the site by removing health threats and restoring contaminated land and water to beneficial uses, remedial activities can impact the global climate through high energy use, release of greenhouse gases, and the generation of waste. It is important to try to balance the cost and benefits to the local and global communities by considering sustainable strategies that reduce total carbon emissions during cleanup activities. This chapter is intended to provide a brief, general framework for using strategies, practices, and technologies that reduce the environmental footprint of LUFT cleanups.

First and foremost, the State Water Resources Control Board (State Water Board) is concerned with meeting all statutory and regulatory requirements for LUFT cleanups. Additionally, the State Water Board encourages the use of environmentally responsible cleanup strategies for corrective actions. The UST Cleanup Fund (USTCF or “Fund”) has reimbursed green cleanups when such strategies are consistent with the “eligible, reasonable, and necessary” corrective-action cost standards the Fund uses to determine cost reimbursement (see the Fund Cost Guidelines section in the UST Cleanup Fund chapter of this Manual and Reimbursable Costs section of the Fund’s Program Summary: http://www.waterboards.ca.gov/water_issues/programs/ustcf/docs/claim_application_forms/program_summary.pdf.) Environmentally responsible strategies can be integrated into cleanup actions using a range of practices and technologies, as shown below, in the associated reference documentation, and in standard guides.

RPs who implement environmentally responsible cleanups should seek opportunities to optimize and encourage innovations related, but not limited, to the following areas:

- Reducing energy use
- Reducing the generation of air pollution and emission of greenhouse gases
- Reducing water use and impacts to water resources
- Considering land use and protection of ecosystems
- When generating waste: Reduce, Reuse, and Recycle materials and waste

Environmentally responsible strategies should be considered for all stages of the cleanup process, including site assessment, system design and installation, system operation, and site closure. The scope of applicability of green options can vary, from considering the direct impacts of on-site activities and transportation to performing a life-cycle analysis of the cleanup. However, due to the relatively small size of LUFT sites and fairly uniform remediation options, the most efficient way to proceed is usually towards a quick and simple analysis which, at a minimum, considers direct impacts to the environment and impacts from transportation.

Quantitative calculators or life-cycle analysis tools can be used to apply measures during remediation to maximize environmental sustainability benefits. These tools can help analyze the manufacture, use, and transport of materials, products, equipment, and wastes associated with all phases of a cleanup. They may allow for quick and easy identification of those activities with the most significant impacts. The results of a life-cycle analysis can illuminate ways to reduce environmental impact with minor to moderate changes.

Practices, Strategies, and Technologies to Support Environmentally Responsible Cleanups

Energy Use

- Minimize energy consumption (e.g., use energy-efficient equipment)

- Power cleanup equipment through on-site renewable energy sources
- Purchase commercial energy from renewable resources
- Adapting soil and groundwater remediation systems using less petroleum-intensive power generation

Air Toxics and Greenhouse Gas Emissions

- Minimize use of heavy equipment
- Maximize use of machinery equipped with advanced emission controls
- Use cleaner fuels to power machinery and equipment
- Sequester carbon dioxide onsite (e.g., soil amendments, re-vegetation)
- Minimize dust generation and airborne transport of contaminants
- Minimize number of trips to the site and number of vehicles required for cleanup

Water Use and Impacts to Water Resources

- Minimize water use and depletion of natural water resources
- Capture both clean and treated water for reuse (e.g., aquifer recharge, irrigation, consumption)
- Minimize water demand for re-vegetation (e.g., native species)
- Employ best management practices for stormwater

Land Use and Protection of Ecosystems

- Integrate anticipated site use or reuse plans into the cleanup strategy
- Minimize areas requiring activity or use limitations (e.g., destroy or remove contaminant sources)
- Minimize unnecessary soil and habitat disturbance or destruction
- Restore or create habitat using native species and local materials (e.g., rock)
- Minimize noise and lighting disturbance
- Prevent the release of contaminants

Waste Management: Reduce, Reuse, and Recycle Materials and Waste

- Minimize consumption of virgin materials
- Minimize waste generation
- Use recycled products
- Segregate and reuse or recycle materials

References

California Department of Toxic Substances and Control (DTSC). 2009. Interim Advisory for Green Remediation. Available at: http://www.dtsc.ca.gov/omf/grn_remediation.cfm

U.S. EPA Office of Solid Waste and Emergency Response (OSWER). 2009. Principles for Greener Cleanups. Available at: http://www.epa.gov/oswer/greenercleanups/principles.html

U.S. EPA Region 9. 2009. Greener Cleanups Policy. Available at: http://www.epa.gov/region9/climatechange/pdfs/greener-cleanups-policy.pdf

Section 2: Initial Response, Reporting, and Tank Removal

Chapter 10: Initial Reporting and Abatement

September 2012

Scope of This Chapter

Federal and State agencies require owners or operators to respond to an unauthorized release from an underground storage tank (UST). This chapter provides owners and operators a guide on how to identify and confirm a release and determine what steps to take as an immediate response to stop further impacts to the surrounding environment.

An unauthorized release, as defined by California Health and Safety Code (H&SC) §25295, is a release which 1) escapes from a UST's secondary containment, or from the primary containment, if no secondary containment exists, 2) increases the hazard of fire or explosion, or 3) causes any deterioration of the secondary containment of the underground tank system.

An unauthorized release can happen at any moment—during tank fueling or by failure of a tank wall, from the piping, at the dispensers, or from waste-oil tanks at service stations. Regardless of how or where the unauthorized release occurs, it is the responsibility of the owner or operator to respond and to report the release to state and/or federal agencies.

Initial Response

Once an unauthorized release is detected, the first step is to take immediate action to stop the leak and prevent further release. This may require removing the residual product from the equipment in question. It is critical to determine whether or not any fire, explosion, or vapor hazards are present and, if so, to mitigate them.

Tank owners or operators shall provide an initial report to the local agency within 24 hours and then follow up with a full written report within five working days. Owners and operators shall transmit information regarding an unauthorized release to the local agency on a written form or using an electronic format developed by the State Water Resources Control Board (State Water Board) and approved by the Secretary for Environmental Protection.

Leak Reporting. The Unauthorized Release Form can be downloaded as an Adobe PDF and Microsoft Word document from the State Water Board website: http://www.swrcb.ca.gov/ust/forms/.

The lead agency is determined based on the volume of the spill and the impacted medium/media. The responsible party (RP) first reports to the agency that has issued UST-related permits at the affected site, usually the local Hazardous Materials agency (Certified Unified Program Agency [CUPA]), which may also act as a Local Implementing Agency (LIA), or the Local Oversight Program (LOP) for soil and groundwater investigation and remediation, to determine whether one of them has jurisdiction over the release. If the local Hazardous Materials agency is not an LIA or LOP (or located within the geographic boundaries of an LIA or LOP), the case will fall under the jurisdiction of the Regional Water Quality Control Board.

Legal.

As defined in the UST Regulations, California Code of Regulations (CCR) Title 23, Division 3, Chapter 16, Article 5, §2650, the owners or operators shall report to the local agency any unauthorized release described in Sections 25295 and 25295.5 of the California H&SC.

AB 358 (Ch. 571, Stats. of 2011) requires that owners or operators transmit certain information regarding an unauthorized release to the local agency on a written form or using an electronic format developed by the State Water Board and approved by the Secretary for Environmental Protection.

Reporting

An Unauthorized Release Report needs to include information regarding an unauthorized release to the local agency on a written form or using an electronic format developed by the State Water Board and approved by the Secretary for Environmental Protection. The report should include, but is not limited to, the following:

- The Facility/Site name, address, and telephone number;
- Discharge date or discovered date, and report date;
- Discharge cause and discharge source
- Any further corrective or remedial actions, including investigative actions, that will be needed to clean up the unauthorized release and abate the effects of the unauthorized release;
- A time schedule for implementing the actions specified above;
- The UST system's record of compliance with California H&SC Chapter 6.7, including data on equipment failures;

Any other information the State Water Board deems necessary to implement or comply with California H&SC Chapter 6.7, Chapter 6.75 (commencing with Section 25299.10), or the 40 Code of Federal Regulations, Subtitle F.

The lead agency may request that the RP conduct an initial site characterization to make a rapid determination of how the release may have occurred and its estimated quantity.

Initial Abatement Actions

Unless otherwise directed by the lead agency, owners and operators are required to perform these initial abatement measures in response to an unauthorized release:

- Remove as much of the substance as possible from the UST system to prevent further impact to the environment;
- Visually inspect for substance release above- and below-ground, and attempt to prevent further substance migration into the surrounding soils and groundwater; and
- Continue to identify, monitor, and mitigate any additional fire or safety hazards posed by potentially migrating vapors or free product from the UST excavation zone.

References

California Code of Regulations (CCR), Title 23, Division 3, Chapter 16, Article 5.

California Health & Safety Code (H&SC), §§25291, 25292, 25294, and 25295.

40 *Code of Federal Regulations*, Subtitle F.

U.S. Environmental Protection Agency (EPA), Office of Environmental Guidance, Resource Conservation and Recovery Act (RCRA) Subtitle I.

Chapter 11: Release Response Prioritization

September 2012

Scope of This Chapter

This chapter discusses the various types of responses that occur as a result of an unauthorized release. The threat to human health, safety, and the environment will determine whether an urgent, interim, or long-term response is appropriate.

Urgent Response

Urgent response includes scenarios where an imminent threat to human health or the environment results from sudden and/or large releases of fuel products, such as a tanker truck or rail car overturning. Because this Manual addresses issues pertaining to leaking *underground* fuel tanks (LUFTs), the most likely urgent-response scenario is a tank breach/failure or a major line loss. Evidence for this event could include light nonaqueous-phase liquid (LNAPL) surfacing or appearing in storm or sanitary sewers or utility conduits, loss of inventory, strong odors/vapors, explosions, or fires. In the event that an imminent threat to human health or the environment exists, public and worker safety is to be protected under the *Code of Federal Regulations* (CFR), Title 29, Chapter 17, Part 1910, Occupational Safety and Health Administration (OSHA).

Remediation in these instances will consist first of emergency response actions, such as immediate containment and recovery of spilled fuels, often in cooperation with local Hazardous Material agencies, fire departments, etc. Remediation of residual impacts will then take place following standard procedures for non-urgent response remedial actions.

Interim Remediation/Rapid Response

Regulatory agencies may concur with interim remediation actions where the risk to human health, safety, and/or the environment may be less than in an urgent-response scenario, but sufficient to warrant rapid actions; for example, to contain a migrating groundwater plume or expanding LNAPL footprint.

Interim remediation should be pursued concurrently with other required site actions, such as lateral plume delineation or bench testing for a final remedy.

In most cases, interim remediation does not supersede the requirement for a formal analysis of final remedies, including submittal of a Corrective Action Plan (CAP). The regulatory case worker may, however, allow interim remediation to stand as the final remedy if it can be demonstrated that interim actions will rapidly achieve remedial goals or until site conditions meet low-threat closure criteria as required by State Water Resources Control Board (State Water Board) Resolution 2012-0016, Low-Threat UST Case Closure Policy, as discussed in the Risk Evaluation and Management Chapter. Proposals for initiation and/or continuance of interim remediation usually take the form of work plans.

Updates on the progress of interim remediation should be included in routine reports, or as otherwise approved by the regulatory agency. For example, a work plan may contain a proposal to conduct interim remediation for six months, followed by a report of findings with recommendations for additional site actions. Check with the regulatory agency for the required reporting documentation, outline, and format.

Examples of interim remediation processes include (but are not limited to):

- Mobile (non-fixed) or temporary treatment systems and processes; for example, free product bailing and skimmer operations.
- Periodic or extended single-event batch extractions.

Rapid response is used where health/environmental risk drivers (e.g., an immediate need for plume containment) or other drivers (e.g., property redevelopment) affect remedial method selection. Examples of rapid-response remediation processes include (but are not limited to) remedial excavation and sustained-batch extraction.

Remedial excavation is effective as a means of removing impacted soils rapidly, but can be *in*effective at addressing groundwater issues, unless a groundwater plume is localized or derives primarily from low-permeability soils.

Sites with widespread groundwater issues may not significantly benefit from remedial over-excavation. In general, remedial excavation can be less cost-effective compared with other remediation processes, except in heavy clay soils with shallow groundwater conditions. Sites like these are often resistant to other forms of remediation. See the Soil Excavation section in the Remediation chapter for situations in which excavation is an effective means of contamination removal.

Longer-Term Response

If interim remediation is not implemented or interim actions do not rapidly achieve remedial goals, a Corrective Action / Remedial Action Plan that contains recommendations for feasible remedial actions shall be submitted to the lead regulatory agency for concurrence.

Feasible remedial actions are often conducted over periods of several months and, in a few cases, may continue for longer periods or until site conditions meet low-threat closure criteria, as required by State Water Board Resolution 2012-0016, as discussed in the Risk Evaluation and Management Chapter. These remedial actions involve fixed remediation equipment connected to public utility lines (natural gas, electricity, sewer, and/or storm drains). Local county/city permits may be required to install the remediation equipment enclosure, subsurface piping, aboveground remediation equipment, and remediation wells. Discharge permits may be required by local air districts, water districts, or state/county/local agencies. Installation of a fixed remediation system normally requires professional engineering and construction contractor planning, design, and oversight. Construction should be completed using a licensed, appropriately trained, and certified contractor.

Construction of fixed remediation systems usually includes installation of underground conveyance piping. Active property use presents challenges to piping installation, as piping must be routed around existing site features but at the same time must also connect to treatment wells installed in the target site areas (e.g., the areas of highest concentrations). Business or occupant / community disruption is unavoidable during construction and should be weighed against other factors when selecting a remediation process.

Examples of longer-term remediation processes include (but are not limited to):

- Soil-vapor extraction (SVE) systems
- Bioventing
- Bio- and air sparging
- Groundwater-extraction systems

See the Remediation chapter for further discussion.

> **Important!** The *California Code of Regulations* (CCR) Title 23, Chapter 16, Article 5, describes the minimum initial response requirements for an unauthorized release.

References

Code of Federal Regulations, Title 29, Chapter 17, Part 1910, Occupational Safety and Health Administration.

California Code of Regulations, Title 23, Division 3, Chapter 16, Articles 5.

California State Water Resources Control Board (State Water Board), Resolution 2012-006, Low-Threat UST Case Closure Policy. Adopted May 1, 2012, effective August 17, 2012.

Chapter 12: Tank Removal and Closure in Place

September 2012

Scope of This Chapter

This chapter provides suggestions on how to remove an underground storage tank (UST) or how to properly close it in place. This chapter also includes guidance on confirmation sampling needed to ensure adequate source removal.

UST Removal or Closure in Place

There are two methods to properly decommission a UST. The first is to completely remove the UST, and the second is to fill it with an inert solid and leave it in place.

If a leak is confirmed and cannot be repaired, it is recommended that the UST and/or piping be removed, depending on the evidence of leakage and specific site features. Most responsible parties (RPs) elect to remove the UST, and this is the method generally preferred by regulatory agencies.

Closure in place is recommended only in cases in which undue damage to nearby utilities or building foundations is of concern, or when regulatory agencies do not approve of UST removal. It is legal to close a tank in place; however, it is generally not recommended due to the possibility of overlooking contamination or complicating future development at the site.

There are several steps that need to be taken to remove or close a UST in place, including field work preparations, UST removal, regulatory inspection during removal, confirmation soil sampling, free-product removal to the maximum extent practicable, and reporting.

Pre-Field Work Considerations

There are several things to consider prior to the actual removal of a UST, including obtaining the proper permits, locating the UST and the associated infrastructure (all piping and appurtenances), ensuring that underground and overhead utilities have been properly located, and properly notifying regulatory/permitting agencies and nearby utility owners prior to mobilization. The Pre-Field Work Considerations section of the Site Assessment chapter is a good source of information to consider prior to mobilizing for field work.

Permitting

Permitting for tank removal varies from site to site and from agency to agency. Generally, local agencies or agency associations, such as a Certified Unified Program Agency (CUPA), have jurisdiction over UST removals and will provide direction on the required permits. Oftentimes, permits will be required from the local fire department, health department, building department, and air quality district, among others. Each permit will have different requirements for notification prior to field work and reporting afterwards.

Utility Locating

California law requires the notification of Underground Services Alert (USA)/Dig Alert at least two (2) full working days prior to digging. Delineation of the proposed excavation site is mandatory. The area to be excavated should be marked with suitable markings. In addition to notifying USA/Dig Alert, it is recommended that a geophysical survey be conducted to verify the existence and location of each UST and delineate on-site underground service lines and infrastructures.

Important! Dial 811 to notify USA/Dig Alert before you dig.

Health and Safety

Health and safety are always of importance when conducting field work and are paramount due to the nature of working with fuel; limited oxygen, toxic gas, and fire and explosion hazards are of real concern. A plan for managing the risk should be considered prior to entering the field. The Health and Safety chapter provides guidance on safety considerations and on preparing Health and Safety Plans.

Field Work

Soil Excavation

Removal of soil from the top and sides of the UST as well as associated piping and appurtenances is required in order to expose the UST. Piping joints and elbows should also be exposed prior to removal to optimize sampling points. While excavating the soil around the tanks, it is important to avoid the use of sparking tools and ignition sources such as static electricity, flames, and open flames. A photo-ionization detector (PID), or similar device, should be used during soil excavation to monitor concentrations of volatile organic compounds (VOCs) in the air. The excavated soil must be stockpiled or containerized for proper disposal or reuse in the excavation, if laboratory analysis indicates reuse to be acceptable.

Tank Decontamination

Decontamination of all liquid, solid, and sludge from the UST and associated piping is necessary before the tank is either removed or closed in place. The waste must be properly disposed of by a licensed waste hauler, and waste manifests must be received from the disposal facility. Monitoring of the UST interior by a Certified Industrial Hygienist, Certified Marine Chemist, or Certified Safety Professional and a “clean certification” is often required prior to tank removal.

Important! It is important that a combustible gas indicator (CGI) be used during tank decontamination to ensure worker safety.

Mitigate Fire/Explosion Hazard

When removing USTs or closing them in place, it is important to mitigate any fire or explosion hazard. If the material that was stored in the UST was flammable and conditions onsite present a fire or explosion hazard, the UST should be rendered inert after decontamination using an inert gas such as nitrogen or carbon dioxide (“dry ice”). This reduces the oxygen content of the “ullage” (the space above the fuel that contains air and fuel vapors) to below the combustion threshold. Without sufficient oxygen in the tank, the fuel vapors in the ullage cannot ignite, and an explosion does not occur.

Tank Removal

A tank is typically removed using a small crane and associated heavy machinery; or by other means after any explosion hazard has been mitigated by rendering the tank inert using dry ice or other means. Generally, a tank-removal contractor with prior experience is hired to ensure successful and safe removal.

Site inspection by local agencies is generally required and typically takes place after the UST and its associated piping are fully exposed. It is the responsibility of the RP to inform the regulatory agency in advance of the removal activities. The tank itself should be treated as contaminated regardless of whether it is to be recycled or disposed (*California Code of Regulations* [CCR] Title 23, Division 3, Chapter 16, Article 7). Regulations vary from jurisdiction to jurisdiction regarding dismantling a UST onsite. In general, a treatment, storage, and disposal (TSD) facility should be used to dismantle, dispose of, and/or recycle a contaminated UST. It is important to contact the lead regulatory agency regarding disposal and recycling options within the specific jurisdiction for the site.

If standing water is encountered in the excavation, a grab sample may be collected; however, groundwater encountered in open excavations tends to be highly disturbed during excavation activities, causing aeration and potentially negative bias in detected constituents of concern (COCs). Conversely, turbidity, sheen, and product globules may lead to positive bias in detected COCs; therefore, the water sample should be used for qualitative purposes only. Soil samples must be collected to confirm the presence or absence of an unauthorized release. See the Confirmation Sampling section below for further details.

Closure in Place

Closure in place is recommended only in cases in which undue damage to nearby utilities or building foundations is of concern. It is generally not recommended due to the possibility of overlooking potential contamination; therefore, if closure in place is elected, it's important to determine whether an unauthorized release has occurred prior to closing the tank. The Confirmation Sampling section below discusses the procedures for collecting confirmation samples.

Upon confirmation that an unauthorized release has not occurred and after regulatory approval has been received, the tank can be filled with an inert material such as cement slurry. A regulatory agency representative is usually required to witness the filling of the tank with inert material.

If an unauthorized release has occurred, additional characterization and remedial action will be necessary prior to closing the tank in place.

Legal.

CCR Title 23, Division 3, Chapter 16, Section 2672(c) provides requirements for UST closure in place.

Confirmation Sampling

When a UST is removed or closed in place, California Health and Safety Code [H&SC] Division 20, Chapter 6.7, Section 25298 requires the UST owner/operator to "demonstrate to the local agency that there has been no significant soil contamination resulting from a discharge in the area surrounding the UST or facility." This is referred to as *confirmation sampling*.

Generally, a regulatory agency representative will be present during tank removal/closure in place to ensure that the proper response actions are implemented if free product or contamination is encountered.

Sampling procedures should be conducted in accordance with guidance provided from the lead regulatory agency.

Legal.

CCR Title 23, Division 3, Chapter 16, Article 7 states that "if an underground storage tank or any portion thereof is removed, soil samples shall be taken immediately beneath the removed portions of the tank, a minimum of two feet into native material at each end of the tank…[and] a separate sample shall be taken for each 20 linear-feet of trench piping." Additionally, H&SC Division 20, Chapter 6.7 authorizes the local regulatory agency to request additional samples as needed.

Sampling for Tank Removal

In general, confirmation samples are collected from potential worst-case locations, including:

- Below each end of the tank invert,
- Below the tank piping (including fittings, valves, elbows, joints, flanges, and flexible connectors),
- Beneath the product dispensers, if removed,
- From stockpiled soil that has been removed from the excavation,
- From areas where visual staining or discoloration is observed, and
- From areas where a vapor-monitoring instrument indicates the highest reading.

To sample below the tank invert, collect samples at a minimum of 2 feet vertically into native soil.

- For tank volumes less than 12,000 gallons—collect one soil sample at each end of the removed tank (two samples total)
- For tank volumes equal to or greater than 12,000 gallons—collect one soil sample at each end of the removed tank and one sample below the center of the removed tank (three samples total)

To sample below the connected piping, collect soil samples from the base of pipe trenches at a minimum of 2 vertical feet into native soil and at a minimum of every 20 feet linearly along connected piping. Soil samples should be collected below each pipe fitting and from any other area where contamination is present or likely to be present, including beneath each removed dispenser, at a minimum of 2 feet vertically. The local regulatory agency may request that additional samples be collected at greater depths. An example of the procedure is shown in Figure 12-1.

If standing water is encountered in the excavation, it may be necessary to collect a water sample for laboratory analysis. Prior to sampling, the water may be vacuumed from the excavation. If groundwater flows back into the excavation, it is necessary to collect a sample to determine if a release may have occurred and to characterize the water for disposal. This both confirms that the water is actually groundwater and provides a sample from a source that was relatively undisturbed by the UST removal process. Groundwater encountered in open excavations tends to be highly disturbed during excavation activities, causing aeration and potentially negative bias in detected COCs. Conversely, turbidity, sheen, and product globules may lead to positive bias in detected COCs; therefore, the water sample should be used for qualitative purposes only.

Along the soil stockpile, retrieve one sample per 100 cubic yards of soil linearly and between 2 and 4 feet below the surface of the stockpile. Samples collected from the excavated soil will indicate whether the soil should be disposed of as a regulated waste or if it can be reused in the excavation.

All samples should be analyzed for applicable COCs using approved methods. See the chapter on Laboratory Analysis and Methods: Soil and Groundwater and confirm with the lead regulatory agency.

Tables 12-1 and 12-2 represent a summary of the minimum numbers of recommended samples to be collected during tank removals.

Table 12-1: Summary of Sampling Recommendations at UST Sites: Water Is Not Present

1. Collect samples at a minimum of 2 vertical feet into native soil.
2. If areas of obvious contamination are observed, they are to be sampled.

Tank Size	Minimum No. of Soil Samples	Location of Soil Samples
Less than 12,000 gallons	TWO per tank	One from directly below each opposite end of the tank
Equal to or greater than 12,000 gallons	THREE per tank	One from below the center of the tank and one from directly below each end of the tank
Connected piping	ONE	Every 20 linear feet, and under pipe fittings
Dispensers	ONE	Below each removed dispenser

Notes:

Additional samples may be added to adequately characterize the excavation.

Table 12-2: Summary of Sampling Recommendations at UST Sites: Water Is Present

1. The tank pit may be purged and allowed to refill before sampling. The purged water is to be handled correctly for disposal.
2. The water sample is to be representative of water in the tank pit.

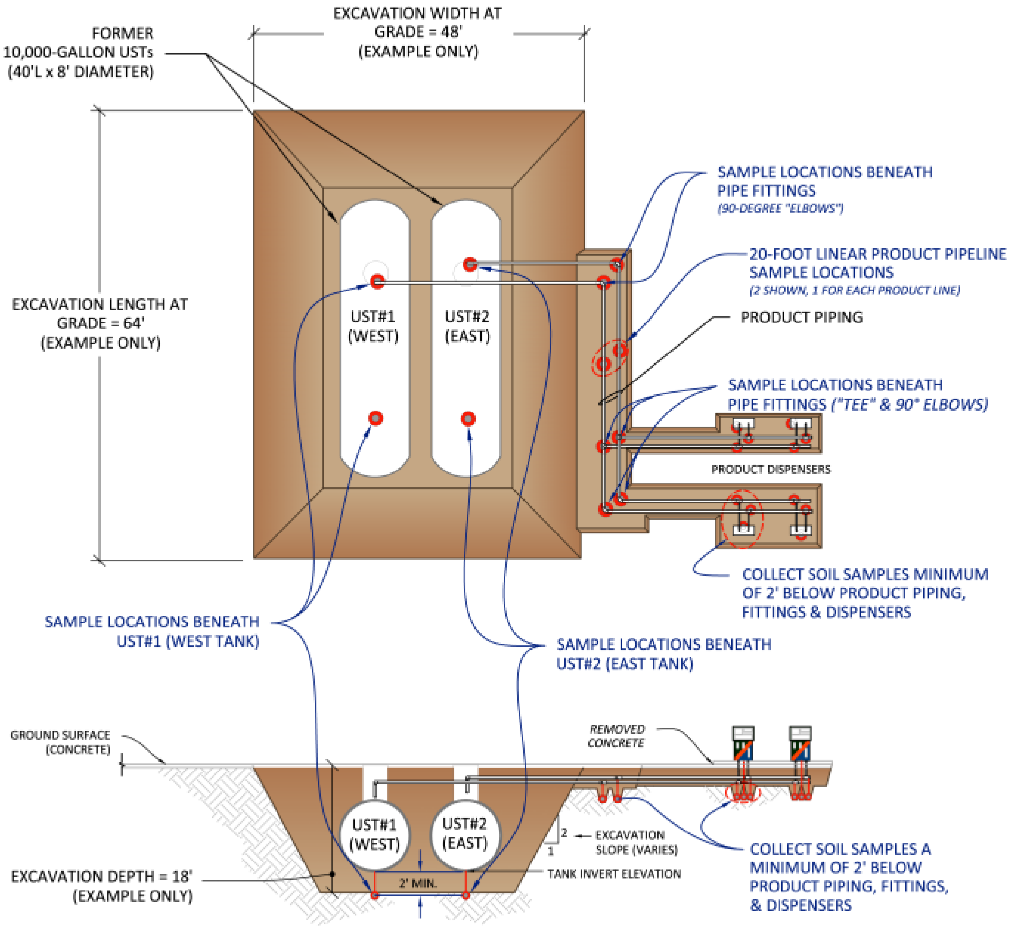
Tank Size	Minimum No. of Soil Samples	Location of Soil Samples	Minimum No. of Water Samples
Less than 12,000 gallons	TWO per tank	One from side wall next to opposite ends of the tank, at the soil/groundwater interface	ONE
Equal to or greater than 12,000 gallons or tank cluster	FOUR per tank	One from side wall next to each end of the tank, at the soil/groundwater interface	ONE
Connected piping	ONE	Every 20 linear feet, and under pipe fittings	N/A
Dispensers	ONE	Below each removed dispenser	N/A

Notes:

Additional samples may be added to adequately characterize the excavation.

N/A: Not Applicable

Figure 12-1: Diagram of Tank Removal Soil Sampling: Water Is Not Present



Sampling for Tank Closure in Place

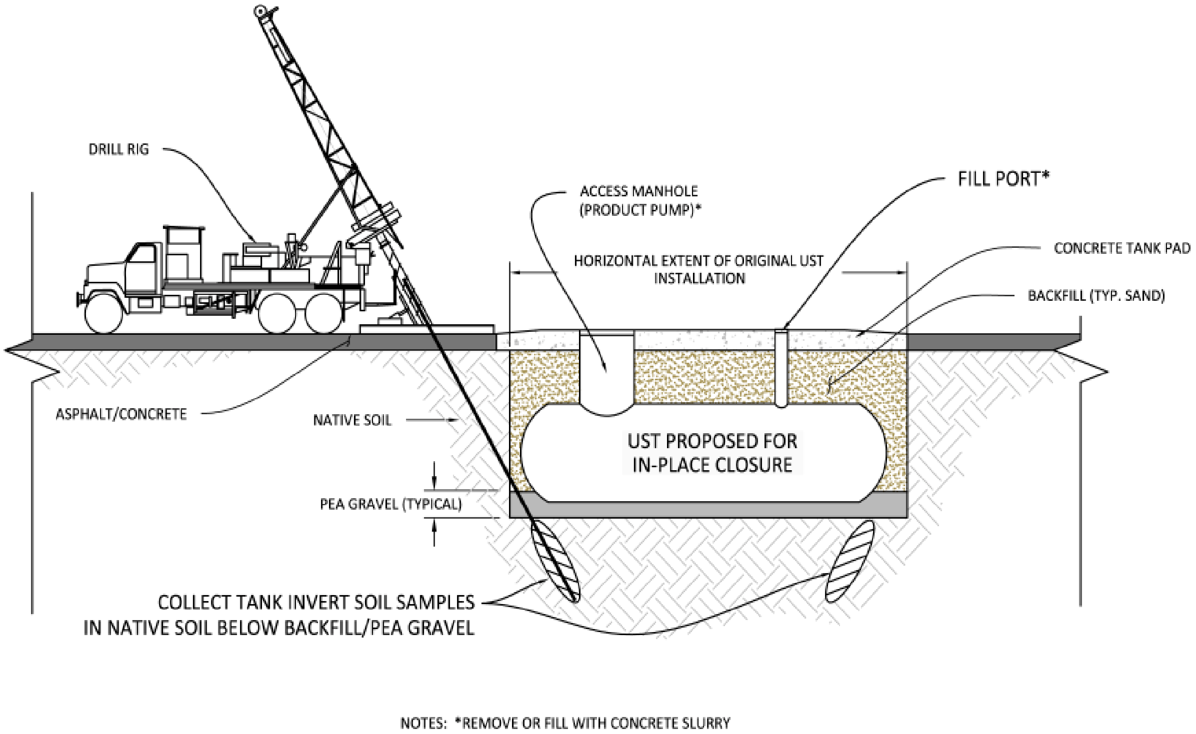
The sample-collection approach for a tank closure in place is different from the approach used for confirmation sampling for tank removal. CCR Title 23, Division 3, Chapter 16, Article 7 states that "if a [UST] or any portion thereof is not removed, at least one boring shall be taken as close as possible to the midpoint beneath the tank using a slant boring… or other appropriate method…as approved by the local [regulatory] agency."

For single tanks (separated from other tanks by at least 20 feet), it is recommended that at least two soil borings be advanced, one at each end of the tank, along the tank's major axis. An example of this procedure is shown in Figure 12-2 below.

It is recommended that soil borings for multiple tanks be placed along a 20-foot interval around a tank cluster (tanks less than 20 feet apart). Please note that this may change, based on actual site conditions. Soil samples should be obtained 2 feet below the tank invert.

Samples should be analyzed for applicable COCs using approved methods. See the chapter on Laboratory Analysis and Methods for Soil and Groundwater.

Figure 12-2: Diagram of Sampling for Tank Closure in Place



SECTION VIEW - ANGLE BORING AND
SAMPLING FOR UST CLOSURE IN-PLACE

Free Product or Contamination Removal

Free product and/or contamination in the excavation can be detected by visual observation (i.e., Light Nonaqueous Phase Liquid [LNAPL] on the water surface), by the use of a PID, or by analytical methods. Samples sent to laboratories should be analyzed for contaminants appropriate to the material stored in the UST; see the chapter on Laboratory Analysis and Methods for Soil and Groundwater.

If the presence of free product and/or contamination is confirmed, removal activities are necessary. Free product shall be removed to the "maximum extent practicable" and "removed in a manner that minimizes the spread of contamination into previously uncontaminated zones by using recovery and disposal techniques appropriate to the hydrogeologic conditions at the site" (CCR Title 23, Division 3, Chapter 16, Article 5, Section 2655). The Low-Threat UST Case Closure Policy (Case Closure Policy), effective August 17, 2012, requires that free product and the secondary source be removed to the maximum extent practicable (State Water Board Res. 2012-0016). Removal should be conducted in accordance with the lead agency's guidance and local regulations, and in a manner that minimizes fire/explosion hazard. Removed product and contaminated soil should be treated as hazardous waste (CCR Title 23, Division 3, Chapter 16, Article 7).

Refer to the Soil Excavation section of the Remediation chapter for further guidance on proper excavation procedures.

Important! A free-product-removal report must be filed with the State Water Board within 45 calendar days of the initial release report.

If free product is encountered and a removal action is necessary, a proper report is required. Per CCR Title 23, Division 3, Chapter 16, Article 7, Section 2655, the report should include the following:

- Name of person(s) responsible for the removal of the free product
- The quantity, type, and thickness of the free-product layer discovered in the excavation
- How the free product was removed from the subsurface
- Whether any discharge took place on- or offsite during the recovery operation, where it took place, treatment applied to it (if applicable), and the quantity of the effluent of this discharge
- The means of disposal of the free product

Legal.

The following regulations govern tank-removal activities in the State of California:

- Health & Safety Code (H&SC) Section 25295
- California Code of Regulations (CCR) Title 23, Division 3, Chapter 16, Articles 5, 7, and 11

References

California Code of Regulations, Title 23, Division 3, Chapter 16, Articles 5, 7, and 11.

California Health & Safety Code, Section 25295.

County of Orange Environmental Health Department. 2005. Guidelines for the Removal of an Underground Storage Tank. February 10.

County of San Diego. 2004. Site Assessment and Mitigation (SAM) Manual, Section 2: Underground Tank Program. February 18, 2004, revised 2009.

State Water Resources Control Board (State Water Board). 1989. Leaking Underground Fuel Tank (LUFT) Task Force. LUFT Field Manual: Guidelines for Site Assessment, Cleanup, and Underground Storage Tank Closure. October.

State Water Board, Resolution 2012-006, Low-Threat UST Case Closure Policy. Adopted May 1, 2012; effective August 17, 2012.

Section 3: Investigation and Remediation

Chapter 13: Fate and Transport of Petroleum in the Subsurface

September 2012

Scope of This Chapter

This chapter presents a discussion on the fate and transport of petroleum fuels and their individual constituents in the subsurface. This chapter will discuss the various types of fuels, the chemical composition of those fuels, and how the different petroleum constituents behave in the subsurface. The partitioning of petroleum constituents from the liquid fuel mixture into air and water is a large factor in whether the petroleum poses a risk to human health or groundwater quality.

One of the most important things to understand about the fate and transport of a petroleum release is that petroleum enters the subsurface as a separate-phase liquid which is a mixture of thousands of constituents. The liquid mixture does not completely mix with or completely dissolve into the water already in the pore spaces, so it remains as a separate liquid. Its "separate-phase" property is similar to that of other releases of relatively low-solubility chemical liquids, but the fact that petroleum is a *mixture* of constituents is unique and affects the fate of those constituents in the subsurface.

Generalized Chemistry of Petroleum and Refined Petroleum Products

Petroleum Chemistry

The chemistry of petroleum is discussed in many references; a good summary is provided in Potter and Simmons (1998).

Crude oil and refined petroleum products are primarily composed of hydrocarbon molecules. Hydrocarbons contain only carbon and hydrogen atoms. These hydrocarbon molecules are divided into two classes:

- Aliphatic compounds
- Aromatic compounds

Hydrocarbon molecules range from simple to complex structures, with a number of different arrangements (or isomers) of molecules with the same number of carbons. As the molecules get larger and contain more carbon atoms, the number of isomers increases exponentially (e.g., a molecule with 6 carbons has 8 theoretical isomers, but a molecule with 10 carbons has 472 theoretical isomers).

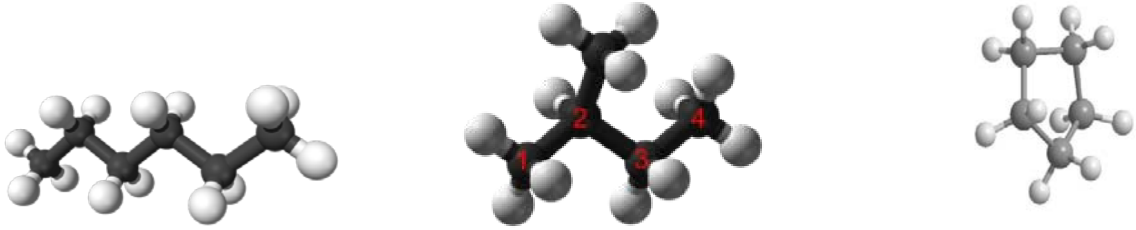
Aliphatic Compounds

In **aliphatic** compounds, carbon atoms are joined together in straight chains (normal), branched chains (iso), or non-aromatic rings (cyclic). They are joined by single bonds (*alkanes*), double bonds (*alkenes*), or triple bonds (*alkynes*). They do not contain ring compounds with double bonds. In the general scientific literature, alternate terms may be used for these compounds. Alkanes are sometimes referred to as "paraffins," and alkenes may be called "olefins."

Alkenes, which occur only in refined petroleum products, have carbon-carbon double bonds, with structures that are normal or branched (Leffler 2000).

The simplest hydrocarbon molecule is methane (CH_4), which has one carbon atom (C) surrounded by four hydrogen atoms (H). Next is ethane, which contains two C's and six H's. Because of their molecular structure, aliphatic compounds have lower solubility than aromatic compounds with the same number of carbons, and, except for *n*-hexane, are significantly less toxic than the aromatics. Examples of aliphatics are shown below in Figure 13-1, with the specific compound name in parentheses.

Figure 13-1: Examples of Aliphatic Compounds



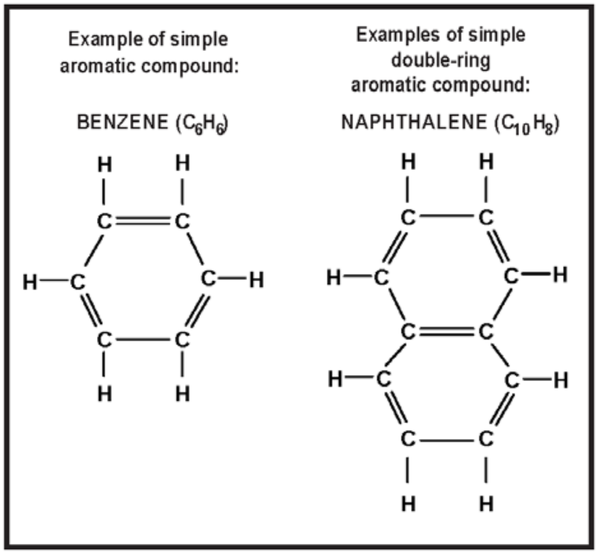
Normal Alkane (n-Hexane): **Branched Alkane (2-Methyl Butane):** **Cycloalkane (Cyclopentane):**

Aromatic Compounds

Aromatic compounds, or aromatics, are unsaturated ring-type (cyclic) compounds (i.e., the ring contains a double bond), and can contain a single ring (mono-aromatic) or multiple rings (polycyclic-aromatic). Aromatic structures are made of carbon rings that are deficient in hydrogen. All aromatics have at least one *benzene ring* (a single-ring compound characterized by three double bonds alternating with three single bonds between six carbon atoms) as part of their molecular structure (see Figure 13-2). Because of their molecular structure, aromatics have higher solubility than aliphatics with the same number of carbons, and are more toxic than the aliphatics.

Benzene is the smallest single-ring aromatic compound; naphthalene is the smallest multi-ring aromatic, with two fused rings as shown below.

Figure 13-2: Examples of Aromatic Compounds



Source: http://www.eoearth.org/article/Hydrocarbon_chemistry?topic=49557

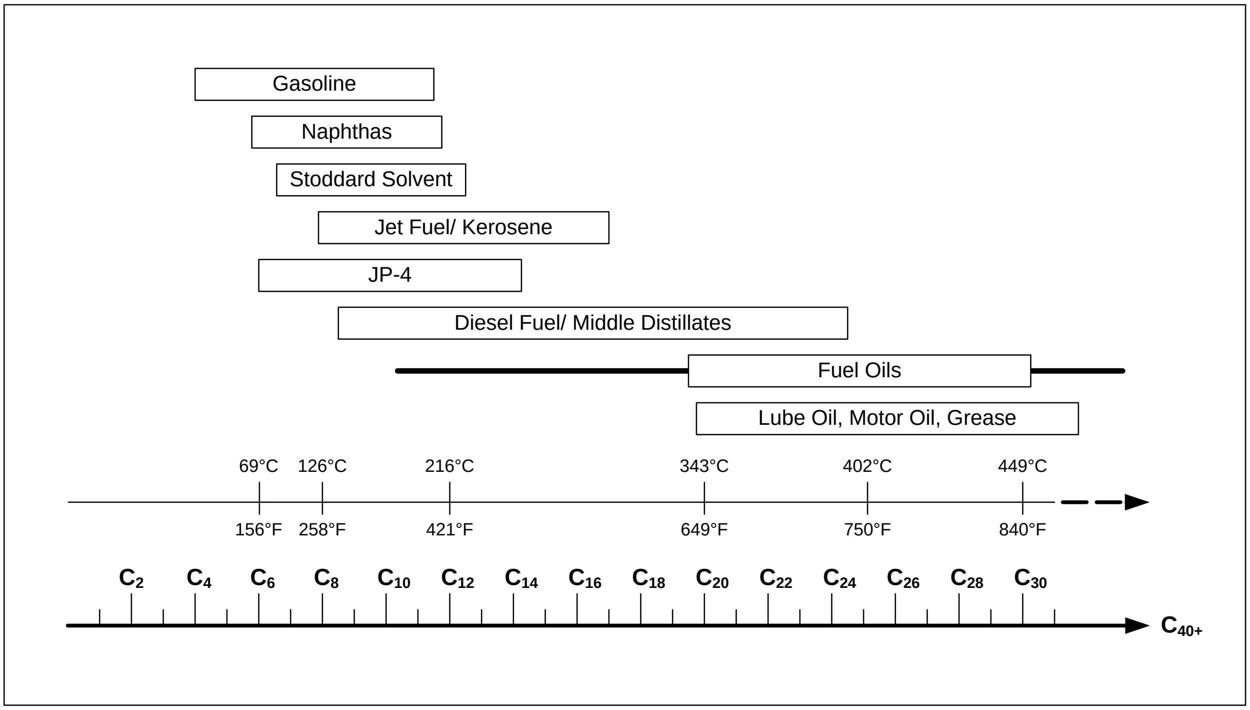
Heterocyclic Compounds

Crude oil and some petroleum products (diesel and heavier) can contain molecules that include nitrogen (N), sulfur (S), and oxygen (O) in their structure; these compounds are often referred to collectively as NSOs. These molecules, also called "heterocyclics," are ring compounds where at least one of the compounds in the ring is not carbon; that is, they are *not* hydrocarbons. The proportion of heterocyclics present in products varies widely, usually in correlation with higher molecular weight.

Composition of Petroleum Products

Crude oil, which contains molecules with the widest range of sizes (e.g., from 2 carbons to more than 40 carbons: C2 to C40+) is refined into petroleum products ranging from gasoline to asphalt. The approximate boiling-point range or carbon range of crude oil and common products is shown in Figure 13-3 below. These refined products are composed of hundreds to thousands of aliphatic and aromatic compounds. The products are refined to meet specifications for either performance in engines (fuels) or specialty products (e.g., lubricating oils, cutting oils, etc.). Additives and blending agents are often added to fuels to improve performance and stability.

Figure 13-3: Approximate Carbon and Boiling Ranges for Petroleum Products



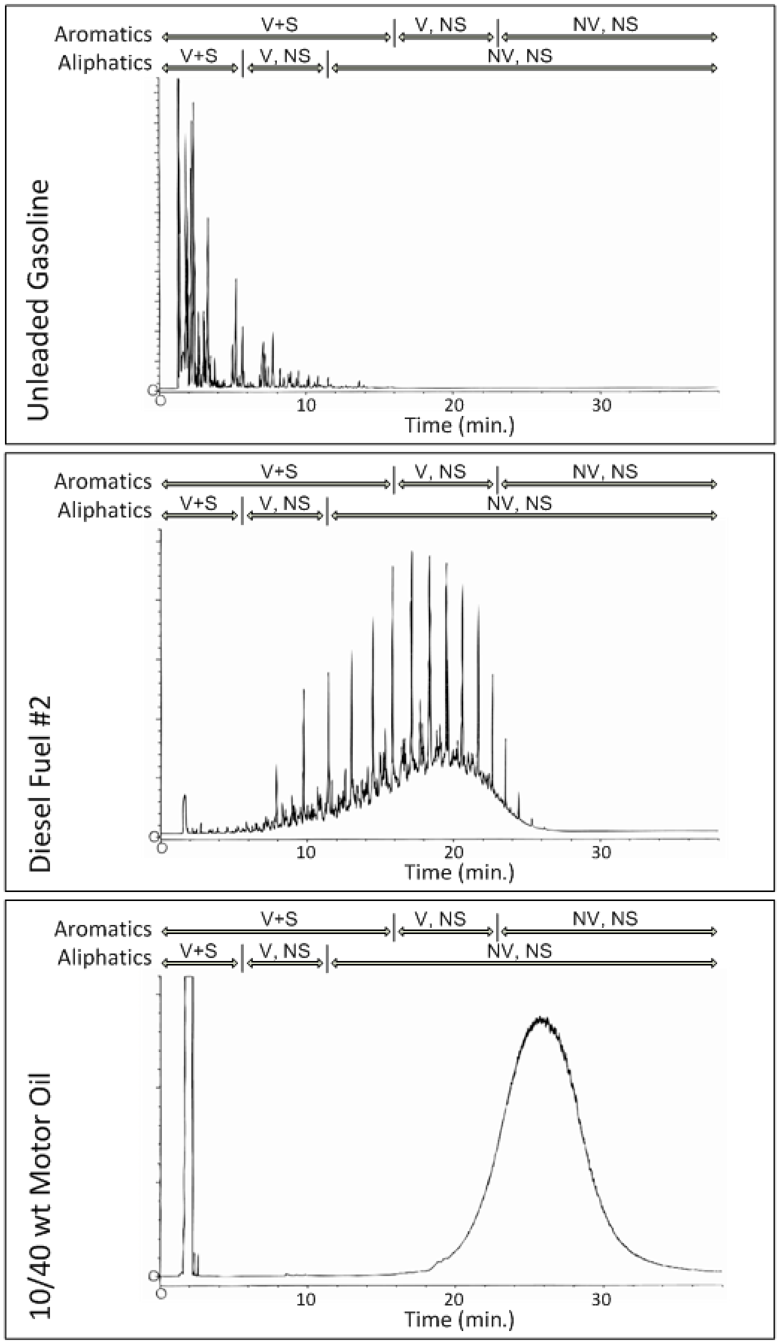
Source: Gustafson et al (1999))

Typical products stored in underground storage tanks (USTs) include:

- Gasoline
- Middle distillates (including diesel and other fuel oils)
- Lubricating oils

Representative gas chromatography–flame ionization detector (GC-FID) chromatograms for gasoline, diesel, and motor oil are shown in Figure 13-4. The *x*-axis on a chromatogram is the retention time (correlated with molecule size) and the *y*-axis is the detector response. The average basic composition of gasoline and diesel is summarized in Table 13-1.

Figure 13-4: GC-FID Chromatograms for Unleaded Gasoline, Diesel Fuel #2, and Motor Oil with Volatility and Solubility of TPH Fractions



Notes:

Time for *n*-alkane carbon number is based on the diesel standard for this set of chromatograms and is approximate. Fraction-specific properties are from Gustafson, et al. (1997) and OR DEQ (2003).

NV	Non-volatile
NS	Non-soluble
S	Soluble (Fraction-specific solubility is greater than 1 mg/L)
V	Volatile (Fraction molecular weight is less than 200 g/mol <u>and</u> Henry's Law Constant is greater than 10^{-5} m^3-atm/mol)

Table 13-1: Average Composition of Fresh Gasoline and Diesel

Component	**Fresh Gasoline (%)**	**Fresh Diesel (%)**
Benzene	2.0 (*max 2.5*)	0.03 (*max 0.1*)
Toluene	8.1 (*max 12*)	0.2 (*max 0.7*)
Ethylbenzene	1.7 (*max 2*)	0.07 (*max 0.2*)
Xylenes	9.0 (*max 11*)	0.5 (*max 0.6*)
Naphthalene	0.25 (*max 0.36*)	0.26 (*max 0.8*)
n-Hexane	2.4 (*max 3.2*)	NM
2-Methylnaphthalene	0.18 (*max 0.29*)	0.89 (*max 1.5*)
HMW PAHs	NM	<0.01
Aliphatics		
C5-C6	21	0
>C6-C8	22	0
>C8-C10	9	2
>C10-C12	3	7
>C12-C16	0	35
>C16-C21	0	34
>C21-C32	0	0
Aromatics		
>C8-C10	13	0.43
>C10-C12	2.3	0.74
>C12-C16	0	8
>C16-C21	0	12
>C21-C32	0	0

Notes:

1. All values in weight (mass) percent. Multiply by 0.01 for mass fraction.
2. Average (and maximum) values for BTEX, naphthalene (N), *n*-hexane, 2-methylnaphthalene, and high molecular weight (HMW) PAHs are from Potter and Simmons (TPHCWG Vol. 2) 1998.
3. TPH fractions are values for fresh (unweathered) "generic" products from Oregon Department of Environmental Quality (OR DEQ; 2003) (revised to include the trimethylbenzenes [TMBs] in the C8-C10 aromatics fraction).

BTEX	Benzene, toluene, ethylbenzene, and xylenes
HMW	High molecular weight
NM	Not measured
OR DEQ	Oregon Department of Environmental Quality
PAH	Polycyclic aromatic hydrocarbon
TMB	Trimethylbenzene

Gasoline

Gasoline is a very complex mixture; it is typically composed of C4 to C12 hydrocarbons (that is, hydrocarbons containing 4 to 12 carbon atoms), with the majority of the mass between C4 and C10. These lighter-weight hydrocarbons include aliphatics and the mono-aromatics (including benzene, toluene, ethylbenzene, and xylenes [BTEX] and the alkylated benzenes like the trimethylbenzenes). Minor amounts of the smallest polycyclic aromatic hydrocarbons (PAHs), naphthalene and methylnaphthalenes, are also usually present. The proportion of various hydrocarbons present is variable and is a function of the refining process and performance specifications. Gasoline also contains additives or blending agents, whose constituents and relative volume have changed over time due to performance criteria and regulatory requirements. These additives/ blending agents include:

1) For leaded automotive gasoline (not sold in California since 1992), the alkylated organic lead species:
    a. tetra methyl lead (TML), tetra ethyl lead (TEL), and related compounds, and
    b. the associated lead scavengers ethylene dichloride ([EDC] or 1,2-dichloroethane [1,2-DCA]) and ethylene dibromide (EDB).
2) For recent and current automotive gasolines, the oxygenates, such as:
    a. methyl tert butyl ether (MTBE, banned in California since 2004),
    b. ethyl tert butyl ether (ETBE),
    c. tert amyl methyl ether (TAME),
    d. di-isopropyl ether (DIPE), and
    e. alcohols, such as t-butyl alcohol (TBA) and ethanol (EtOH).

Research has shown that organic lead species are not typically persistent in the environment unless liquid-phase product is present (Mulroy and Ou 1998).

Other sources of information regarding gasoline composition and its changes since the 1920s are provided in the References section at the end of this chapter (Kaplan and Galperin 1996; Kaplan 2003; Stout, et al. 2002; Stout, et al. 2006).

Middle Distillates – Diesel and Other Fuel Oils

Diesel fuel and fuel oils are much less chemically complex than gasoline, and their components have not changed very much throughout refining history. Fresh diesel fuel #2 (also called fuel oil #2) is composed primarily of C10 to C25 hydrocarbons, which themselves consist largely of aliphatics, with minor amounts of mono-aromatics and PAHs, especially naphthalene and the methylnaphthalenes (EPA 1996). The larger PAHs are generally not found in diesel #2, but can be present in the heavier fuel oils. Fresh fuel oils are abundant in *n*-alkanes but, after weathering, the fuels are dominated by branched and cyclo-alkanes. Other middle-distillate fuels include:

- Kerosene (approximately C8 to C18),
- Kerosene-based jet fuels (e.g., Jet A or JP-5 [C8 to C18] or JP-8 [C8 to C20]),
- Diesel fuel #1 or fuel oil #1 (approximately C8 to C22), and
- Heavier fuel oils such as marine diesel or diesel/fuel oil #4 (approximately C12 to C30).

Bunker fuel (approximately C12 to C35+), also called fuel oil #6 or Bunker C, is the heaviest fuel, and is typically classified as a residual fuel oil. Bunker fuel is very viscous and is frequently “cut” or blended with a diesel-range oil to improve its flow properties.

Because of their larger molecular sizes, middle-distillate fuels tend to be denser, much less volatile, and much less soluble than gasolines. Small aromatics (including BTEX) are generally found only in trace amounts in middle-distillate fuels.

Fuel oils also contain heterocyclic molecules (NSOs) inherited from the crude oil. The typical percent of NSOs increases in heavier fuels: diesel ranges from 0 to 5% NSOs, but fuel oil #6 ranges from 30 to 50% NSOs. The regulatory limits regarding acceptable amounts of sulfur in diesel fuel have changed over time.

Lubricating Oils (Including Waste Oils) and Hydraulic Oils

Lubricating oils are composed primarily of C25 to C32 hydrocarbons, which are almost exclusively aliphatics (branched and cyclic alkanes). Aromatic hydrocarbons are not present in lubricating oils prior to their use in engines. Because of their very large molecular sizes and the fact that they are almost exclusively aliphatic, unused lubricating oils are nearly insoluble in groundwater and are not volatile.

When lubricating oils are used in engines, they pick up fuel components due to cross-leakage in the chambers and often acquire trace concentrations of metals from engine wear ("wear metals") and potentially the larger PAHs. Used lubricating oils can, therefore, contain aromatics, smaller hydrocarbons, and wear metals.

Hydraulic lift tanks containing hydraulic oils were permanently exempted from UST regulation by the California State Water Resources Control Board (State Water Board) in January 1996 due to the technical finding that these base oils present little risk to human health or groundwater quality (State Water Board letter, November 1995; State Water Board "Report on Hydraulic Lift Tanks," February 1995). California Health and Safety Code, Section 25299.2 gives authority to local agencies to regulate hydraulic lift tanks under their own authority.

Physical/Chemical Properties of Selected Individual Constituents, TPH Fractions, and Petroleum Products

A number of properties, including solubility, vapor pressure, density, and viscosity, can affect the mobility and partitioning of liquid-phase petroleum in the subsurface. Thus, the properties of the compounds are extremely important for evaluation of appropriate remedial technologies. A compilation of these properties for selected petroleum constituents, aliphatic and aromatic hydrocarbon carbon-range fractions, and products is provided in Table 13-2 below. In general, as the average molecular size and weight of a product increase, the density increases, the viscosity increases, and the ability of the product to move through the subsurface materials *decreases*.

Solubility is the measure of the ability of a hydrocarbon constituent to dissolve in water. The solubility of an individual petroleum constituent is generally dependent on the hydrocarbon class and the number of carbon atoms present in the compound (solubility within a given class of hydrocarbons decreases as the number of carbon atoms increases), combined with the proportion of the constituent in the whole mixture (see discussion of *effective solubility* below in this chapter).

The tendency of a petroleum constituent to transfer from the liquid-mixture (non-aqueous-phase liquid [NAPL]) phase to the vapor phase is indicated by the **vapor pressure** of the individual compound. Chemicals having higher vapor pressures have a greater tendency to volatilize than those with lower vapor pressures. As with solubility, the volatilization potential of an individual constituent will be dependent on the relative proportion of that constituent in a petroleum mixture. Lower molecular-weight constituents have greater vapor pressure and volatility than higher molecular-weight constituents. The tendency of a constituent to move from the dissolved phase into the vapor phase is predicted by the Henry's Law Constant (H) for that constituent.

Properties of the aliphatic and aromatic carbon-range fractions are provided in this chapter to complete our understanding of the mixture. The aliphatic and aromatic carbon-range fractions shown in this chapter are the same as those used by the petroleum regulatory programs in Washington and Oregon, and also are generally consistent with the fractions used by most other states. These carbon-range fractions are different from those used by Massachusetts. These carbon-range fractions are actually "*equivalent carbon number*" (EC), and are based on retention time on the gas chromatograph (GC) and normalized to the *n*-alkanes. For example, because of its molecular structure, naphthalene (C10 aromatic) has a slightly higher boiling point and elutes later than *n*-decane (C10 aliphatic); the EC for naphthalene is 11.7, and it would be included in the >C10 to C12 aromatics fraction.

Table 13-2: Representative Properties of Selected Constituents, TPH Fractions, and Products

Component	Molecular Weight (g/mol)	Density(1) (g/cm^3)	Dynamic Viscosity(1) (cp)	Pure-Compound / TPH Fraction / Product Mixture Water Solubility(1,6) (mg/L)	Pure-Compound Vapor Pressure(1) (mm Hg)	Henry's Law Constant (2)	Log K_{oc}
Benzene	78.1	0.88	0.6468	1.78 E+03	76	0.23	1.8
Toluene	92.1	0.87	0.58	5.15 E+02	22	0.27	2.3
Ethylbenzene	106.2	0.87	0.6468	1.52 E+02	7	0.32	2.6
Xylenes	106	0.87(2)	0.68	1.8 E+02	9	0.28	2.6
n-Hexane	86	0.70		1.8 E+01	121	5.0	2.9
Naphthalene	128	1.5		3.1E+01/ 1.1E+02	0.08	0.02	3.3
MTBE	88.15	0.74(2)	---	5E+04(2)	251(2)	0.024	1.1
TBA	74.12	0.79		Infinite	41	0.0005	1.6(7)
Water	18.0	0.998(3)	1.14(3)				
Aliphatic Fractions							
Aliphatic C5-C6	81	0.68		3.6E+01	2.7E+02	33	2.9
Aliphatic >C6-C8	100	0.73		5.4E+00	4.8E+01	50	3.6
Aliphatic >C8-C10	130	0.73		4.3E-01	4.8E+00	80	4.5
Aliphatic >C10-C12	160	0.76		3.4E-02	4.8E-01	120	5.4
Aliphatic >C12-C16	200	0.77		7.6E-04	3.6E-02	520	6.7
Aliphatic >C16-C21	270	0.78		2.5E-06	8.4E-04	4,900	8.8
Aliphatic >C21-C34	400	0.78		1.5E-11	3.3E-07	100,000	10.0
Aromatic Fractions							
Aromatic >C8-C10	120	0.87		6.5E+01	4.8E+00	0.48	3.2
Aromatic >C10-C12	130	0.90		2.5E+01	4.8E-01	0.14	3.4
Aromatic >C12-C16	150	1.02		5.8E+00	3.6E-02	0.053	3.7
Aromatic >C16-C21	190	1.23		6.5E-01	8.4E-04	0.013	4.2
Aromatic >C21-C34	240	1.28		6.6E-03	3.3E-07	0.00067	5.1
Common Petroleum Products							
Automotive Gasoline	100 – 105	0.72 – 0.76(4)	0.63(3)	>100	---	---	---

Table 13-2: Representative Properties of Selected Constituents, TPH Fractions, and Products (Continued)

Component	Molecular Weight (g/mol)	Density(1) (g/cm^3)	Dynamic Viscosity(1) (cp)	Pure-Compound / TPH Fraction / Product Mixture Water Solubility(1,6) (mg/L)	Pure-Compound Vapor Pressure(1) (mm Hg)	Henry's Law Constant (2)	Log K_{oc}
Jet Fuel (JP-4/JP-5)	165 (USEPA on-line)	~0.75	~0.83	15 – 65	---	---	---
Kerosene	170 (OSHA)	0.84(3)	2.30(3)	---	---	---	---
#2 Diesel	233 (USEPA on-line)	0.83 – 0.87(3)	2.70(3)	3 –5	---	---	---
#6 Fuel Oil	>250(5)	0.87 – 0.95	14.5 – 493.5(4)	6	---	---	---
Crankcase Oil	>250(5)	0.84 – 0.96(3)	~275(4)	-<1	---	---	---
Prudhoe Bay Crude Oil	>300(5)	0.91(3)	68.4(3)	---	---	---	---

Sources: American Petroleum Institute (API) 1996; EPA 1996; Lyman and Noonan 1990; Moyer 2003; EPA Regional Screening Levels (RSLs) (chemical properties sheet downloaded June 2010 [EPA 2010]); OR DEQ 2003. Diesel solubility reported in one study as up to 40 mg/L (Potter 1996).

Notes:
1. Values are given at 20°C unless noted.
2. Value is at 25°C.
3. Value is at 15°C.
4. Value is at 38°C.
5. Rough estimate from TPH fraction composition.
6. Naphthalene solubility shown as solid (31 mg/L) and sub-cooled liquid (112 mg/L).
7. Log K_{oc} is unreasonably high, given Log K_{ow} of 0.35 (Moyer 2003).

cp	centiPoise
g/cm^3	Gram per cubic centimeter
g/mol	Gram per mole
K_{oc}	Soil Organic Carbon-Water Partitioning Coefficient
K_{ow}	Octanol-Water Partitioning Coefficient
mg/L	Milligram per liter
mm Hg	Millimeter of mercury
MTBE	Methyl tert butyl ether
OSHA	Occupational Safety and Health Administration
TBA	t-Butyl alcohol
TPH	Total petroleum hydrocarbons
USEPA	U.S. Environmental Protection Agency

Migration of LNAPL

September 2012

When released to the environment, the petroleum enters the soil and exists in the soil pore spaces as a separate liquid-phase mixture that is lighter than water and that does not mix with or completely dissolve into the pore water. This is known as a “Light Nonaqueous Phase Liquid” (LNAPL). The LNAPL occupies the pore spaces in the soil (or fractures in rock) along with water and air. This means that the LNAPL has to displace the water and air in the pore spaces to move. The constraints acting against the LNAPL movement are a function of the relative amounts of the LNAPL, water, and air in the pore spaces; the viscosity/density of the LNAPL; the interconnectedness of the pore spaces; and capillary forces. Movement of LNAPL in the subsurface is very complex, and is described in many publications, including ASTM E2531-06 (ASTM 2006), EPA 1995a, and Interstate Technology & Regulatory Council (ITRC) 2009. Simply put, if enough LNAPL is present in the pore spaces to overcome the capillary forces, the LNAPL will be mobile and can potentially migrate; this is known as “mobile LNAPL” or “free LNAPL” or “free product.” Mobile LNAPL can migrate if a driving head is present; this is known as “migrating LNAPL.” If insufficient LNAPL is present in the pore spaces to overcome the capillary forces, the LNAPL will not be mobile and cannot migrate; this is known as “residual LNAPL” or “immobile LNAPL.” Varying amounts of residual LNAPL trapped in the soil pore spaces represent the primary physical state of what is generally referred to as “impacted soil” in the vicinity of source zones. The following paragraphs provide a more detailed discussion of LNAPL migration in the vadose zone and in the capillary fringe/smear zone.

Migration in the Vadose Zone

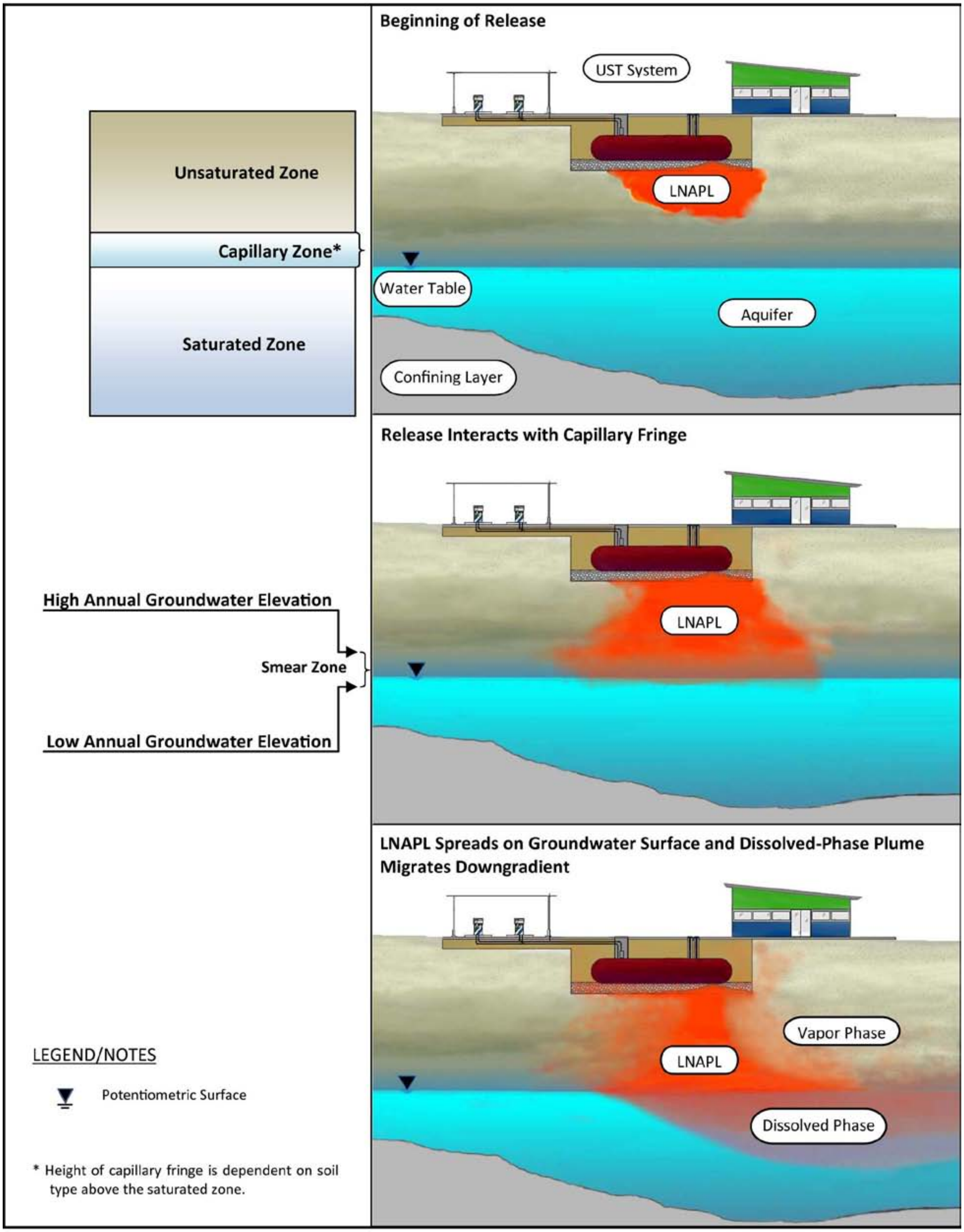
Following a petroleum release, LNAPL moves vertically downward through the unsaturated zone in response to gravity and capillary forces. The rate of migration is determined primarily by the stratification and permeability of the native soil materials. Some horizontal spreading will occur within the vadose zone as vertical migration proceeds because of capillary forces between the LNAPL and solid granular surfaces, the varying hydraulic conductivities of subsurface materials, and horizontal geological features such as bedding planes or fractures.

Several factors, including the volume of the release, rate of the release, hydraulic conductivity of the soils, depth to the water table, and adsorptive capacity of the subsurface materials, will determine whether LNAPL will ultimately migrate downward to the area of the capillary fringe and the water table or remain entirely in the vadose zone. As LNAPL passes through the unsaturated zone, some LNAPL will remain behind in a residual (immobile) state, having been trapped by capillary forces (EPA 1995a; API 1996; Day 2001). This residual LNAPL in the vadose zone can be a source of dissolved-phase constituents to pore water and/or volatilized constituents to soil vapor.

Migration in the Capillary Fringe/Smear Zone

If a sufficient volume of LNAPL is released, it will migrate through the vadose zone, the capillary fringe, and to the water table (see Figure 13-5). As the LNAPL flows downward by gravitational forces through the unsaturated vadose zone, it enters pore spaces that are of increasingly higher water saturation known as the *capillary fringe*. The capillary fringe is defined as the partially saturated zone where groundwater seeps up from the water table due to capillary forces. It is the intermediate zone between unsaturated and saturated conditions. Vertical or lateral movement of LNAPL through pore spaces of increasing water saturation at the capillary fringe depends on displacement of water within the pore spaces. This interface results in lateral migration of the LNAPL. The extent of lateral migration of LNAPL is controlled by the LNAPL head distribution and the relative saturation of LNAPL in the pore space. Because the soil pore spaces also contain water, LNAPL can never occupy 100% of the pore space in the capillary fringe or saturated zone.

Figure 13-5: Progression of a Typical Petroleum Product Release from an Underground Storage Tank



Beginning of Release

Release Interacts with Capillary Fringe

LNAPL Spreads on Groundwater Surface and Dissolved-Phase Plume Migrates Downgradient

LEGEND/NOTES

▼ Potentiometric Surface

* Height of capillary fringe is dependent on soil type above the saturated zone.

In general, migration may be expected to be greatest in the direction of groundwater flow. Increasing LNAPL head or pressure is generally required to displace water within these zones, and LNAPL can migrate some distance below the water table if the pressure head and LNAPL relative saturation are great enough. LNAPL will stop migrating when the pressure head is reduced and when the relative saturation of LNAPL becomes low enough.

The distribution of LNAPL, water, and air in the pore spaces at the capillary fringe/water table is very complex. Once the LNAPL equilibrates at the capillary fringe/water table, it will be mobile (e.g., will flow into a monitoring well) if the relative saturation of LNAPL is high enough. Accumulations of LNAPL at or near the water table are susceptible to smearing within a vertical interval from fluctuations in water-table elevation due to seasonal changes or tidal influence (see Figure 13-6). LNAPL collected at the capillary zone will move downward as the water table drops because the soil pores drain off water, which allows the LNAPL to migrate downward. This leaves residual LNAPL in the expanded unsaturated zone above the new water table and an accumulation of LNAPL at the new capillary fringe. A subsequent rise of the water table will cause the capillary fringe and mobile LNAPL (if any) to move upward. Residual LNAPL can remain in the saturated zone below the raised water table because it is trapped behind water-filled pore spaces. This process results in LNAPL being distributed vertically between limits of high- and low-water levels and is called the *smear zone* (EPA 1995a; API 1996). This residual or mobile LNAPL in the smear zone can be a source of dissolved constituents to groundwater and volatilized constituents to soil vapor.

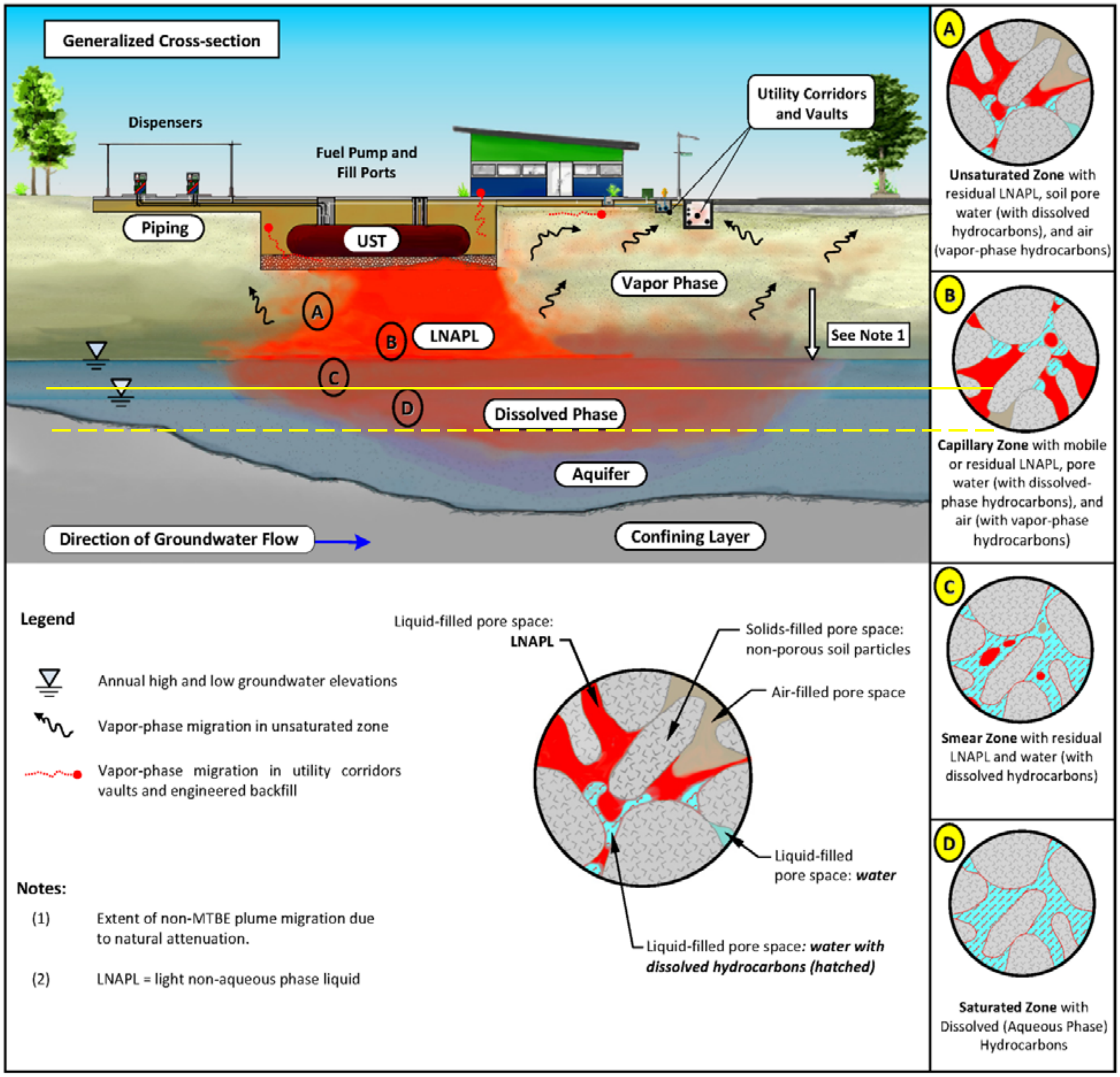
Monitoring wells screened across the smear zone and water table will allow LNAPL in the capillary fringe to separate from the pore water and enter the well because the well provides low resistance to entry of the LNAPL. The accumulation of LNAPL in the well gives the false impression that there is a distinct layer of LNAPL on the water table. The actual distribution of LNAPL in the subsurface outside the well is complex, and the apparent thickness in a well is a poor indicator of the thickness of mobile LNAPL in the soil. The thickness in the soil is always less than the “apparent thickness” in the well. The apparent thickness of LNAPL in a well will change with fluctuating water levels. At times of high water levels, the apparent thickness decreases because more of the LNAPL in the smear zone is trapped behind water-filled pore spaces and cannot migrate into the well. At times of low water levels, the apparent thickness increases because the pore-water saturation decreases within the smear zone now above the water table, which means the LNAPL relative saturation increases, which allows the LNAPL to migrate into the well.

Concept of Residual Saturation and Limits of LNAPL Mobility

As discussed above, LNAPL mobility is a function of its relative saturation, the soil pore type, and LNAPL viscosity. An important practical issue for LUFT sites is the question of, “At what concentration would the LNAPL potentially be mobile in the vadose-zone soil (flow due to gravitational force)?” This is known as *residual saturation*, and it is the concentration above which LNAPL may be mobile and below which LNAPL will not be mobile because it is trapped by capillary forces. Finer-grained soils result in a higher residual saturation concentration for a given LNAPL type, and more viscous LNAPLs result in higher residual saturation concentrations for a given soil type. There have been many studies evaluating the residual saturation concentrations for various LNAPLs in various soil types, and a good summary on the subject is the paper by Brost and DeVaull (2000). This paper recommends screening levels for residual saturation concentrations for various product types. The default soil type for the screening levels was medium to coarse sand. Brost and DeVaull’s screening-level (i.e., measured in coarse-grained material) residual saturation concentration for gasoline was 3,000 milligrams per kilogram (mg/kg); for diesel (“middle distillates”) it was 8,000 mg/kg; and for fuel oils it was 17,000 mg/kg.

However, the detailed data in Brost and DeVaull (2000) show that, as the soil type ranged from coarse gravel to silt, the residual saturation concentrations ranged from 1,000 to 10,000 mg/kg (for gasoline), from 2,300 to 23,000 mg/kg (for diesel), and from 5,100 to 51,000 mg/kg (for fuel oil). Therefore, it is very important to consider soil type when estimating a residual saturation concentration and potential LNAPL mobility at a LUFT site. The data from Brost and DeVaull (2000) are summarized in Table 13-3 below. Site-specific residual saturation concentrations can also be determined by the testing of soil cores.

Figure 13-6: Vertical and Horizontal Distribution of Hydrocarbon Phases



Note that "residual saturation" is not the same as "Csat." "Csat" is not used in this Manual, but is often found in tables of guidance documents or other references for partitioning calculations or risk assessments. "Csat" is a theoretical concentration that represents the condition when all compartments of the soil (solid, air, and water) are "saturated" (or have reached their maximum equilibrium partitioning limits) and, therefore, above which a separate-phase liquid may be present in the soil pore spaces. For petroleum, "Csat" values are quite low because the effective solubility of petroleum is low. For petroleum, which is released to the subsurface as a LNAPL, the LNAPL is typically present in the soil pore spaces; therefore, the "Csat" values are often exceeded, but that does not mean that the LNAPL is "free" or mobile. "Residual saturation" is the concentration above which a LNAPL may be mobile in the soil. For petroleum, residual saturation values are typically several orders of magnitude higher than "Csat" values.

Table 13-3: Example Residual Saturation Concentrations for Gasoline, Diesel, and Fuel Oil in Various Soil Types

Soil Type	Gasoline (mg/kg)	Diesel (mg/kg)	Fuel Oil (mg/kg)
Coarse gravel	1,000	2,300	5,100
Coarse sand and gravel	1,700	3,900	8,700
Medium to coarse sand	3,400	7,700	17,400
Fine to medium sand	5,800	13,000	30,000
Silt to fine sand	10,000	23,000	51,400

Source: Brost and DeVaull (2000)

Notes:

1. "Residual saturation" is the concentration above which the product may be mobile in the respective soil type in the vadose zone via gravity flow, and below which the product is unlikely to be mobile in the respective soil type.
2. Residual saturation concentrations for the products (rounded) are from Table 13-2 of Brost and DeVaull (2000). For the purpose of the LUFT Manual, concentrations are equivalent to "TPH" (either gasoline-range organics [GRO] or diesel-range/oil-range organics [DRO/ORO]).
3. "Middle distillates" in Brost and DeVaull (2000) are shown as "Diesel" in this table.

LNAPL Migration through Man-Made Pathways

LNAPL can also move through man-made preferential pathways, such as improperly grouted monitoring wells, trenches containing distribution piping or utilities, or the backfill of trenches.

Chapter 13: Fate and Transport of Petroleum in the Subsurface

Dissolution of Petroleum Hydrocarbons into Water

September 2012

Crude oils and refined products are extremely complex mixtures containing from hundreds to thousands of constituents. The portion of a fresh petroleum mixture (e.g., LNAPL) which is soluble and therefore dissolves into water consists of significantly fewer constituents, because the dissolved phase is a function of *effective* (as opposed to pure-phase) *solubility* of each individual constituent. This effective-solubility phenomenon is critical to understanding the partitioning of soluble constituents from the LNAPL to pore water (in the vadose zone) or groundwater. Effective solubility of petroleum mixtures is discussed in the literature. Key references include Cline, et al. 1991; Lee, et al. 1992; Shiu, et al. 1990; Mackay and Shiu 1992; Chen, et al. 1994; O'Reilly, et al. 2001; Huntley and Beckett 2002; and Zemo 2006. This section discusses the constituents found within the dissolved phase of various products and the expected concentrations of each of those constituents.

Pure-Compound Solubilities

Within a given molecular class, lower-molecular-weight petroleum constituents usually have higher pure-compound solubilities (Gustafson, et al. 1997; Mackay and Shiu 1992; Yaws, et al. 1990). Aliphatics have low pure-compound water solubilities at molecular weights exceeding six carbon atoms (C6). Mono-aromatics (BTEX and alkylated benzenes) have higher pure-compound water solubilities, with the lowest molecular-weight compound (C6: benzene) having the highest relative pure-compound solubility. The lower molecular-weight PAHs (e.g., naphthalene [C10]) have low to very low pure-compound water solubilities, with the higher-molecular-weight PAHs (e.g., benzo(a)pyrene [C20]) being virtually insoluble in water.

For comparison, the following table shows the solubilities of various arrangements of C6 and C10 compounds. Note how the solubility of aliphatics is much lower than that of aromatics, even those with the same number of carbon atoms.

Table 13-4: Solubility of Various C6 and C10 Compounds

Aromatic		Aliphatic	
Name	**Solubility (mg/L)**	**Name**	**Solubility (mg/L)**
C6 (Benzene)	1780	C6 (*n*-Hexane)	9.5
C10 (Naphthalene)	31 or 110	C10 (*n*-Decane)	0.052

Source: Solubilities from Gustafson, et al. 1997; Mackay and Shiu 1992; Yaws, et al. 1990. Sub-cooled liquid solubility 110 mg/L also shown for naphthalene.

Effective Solubility

The composition and concentration of the dissolved phase (sometimes called the "water soluble fraction," or WSF) from a mixture are controlled by the *effective solubility* of each constituent in the mixture. The effective solubility of each constituent is a function of its:

- Pure-compound solubility in water
- Mole-fraction within the mixture

Effective solubility dictates that the equilibrium concentration of each constituent within the dissolved phase of a petroleum product is significantly less than its pure-compound solubility, which means that, as a mixture, the individual components of the petroleum products are less able to dissolve into groundwater than those components would be if they were the only compound present. For the purpose of this LUFT Manual and in much of the literature, the term "mole fraction" is used interchangeably with "mass fraction" because the data for constituents are typically reported in weight percent or mg/kg. This does not introduce much error into calculations for lower molecular-weight fuels such as gasoline, but may introduce error for the higher molecular-weight fuels (i.e., diesel and heavier).

Drilling Down.

The effective solubility of petroleum constituents has been shown to follow Raoult's Law for ideal mixtures,

$$C_i = X_i * S_i$$

Where

C_i = solute concentrations of component *i* (mg/L)

X_i = mole fraction of component *i*

S_i = aqueous solubility of component *i* (mg/L)

and has been documented for petroleum in the literature (e.g., Cline, et al. 1991; Lee, et al. 1992; Shiu, et al. 1990; Mackay and Shiu 1992; Chen, et al. 1994; O'Reilly, et al. 2001; Huntley and Beckett 2002). The validity of these theoretical estimates and of the effective-solubility approach is supported by the laboratory research described below.

Composition of the Dissolved Phase from Laboratory Studies

The composition of the dissolved phase from fresh petroleum products (including gasolines, kerosenes, jet fuels, diesels, Bunker C fuel, and motor oils) and fresh crude oils has been investigated under laboratory conditions by several researchers using various analytical methods (e.g., Coleman, et al. 1984; Shiu, et al. 1990; Thomas and Delfino 1991; Bruya and Friedman 1992; Chen, et al. 1994; and Potter 1996).

The results from all of these studies are consistent, and provide clear evidence that the petroleum hydrocarbons which comprise the measurable dissolved phase of fresh crude oil and fresh refined products are limited primarily to these discrete constituents:

- C6 to C11 mono-aromatics (BTEX and the alkylated benzenes)
- C10 to C14 PAHs (naphthalene, alkylated naphthalenes, acenaphthene, fluorene, phenanthrene, and anthracene)
- C6 and smaller aliphatics

These studies focused on the hydrocarbon constituents in the dissolved phase of fresh crude oil and fresh refined products; however, these same constituents would also be present in the dissolved phase of weathered products up to the point of their effective solubility. As the constituent dissolves out of the weathered mixture, its mole fraction decreases and therefore its effective solubility decreases; at some point, the constituent will no longer be measureable in the dissolved phase (discussed in detail later).

Blending agents or additives which are polar in their molecular structure, such as oxygenates, have both relatively high pure-compound solubilities *and* large mole-fractions within the product mixture; therefore, they can represent a large proportion of the dissolved phase of a given product. This is why MTBE can be present in plumes in much higher concentrations than the hydrocarbons. Note that polar molecules have slightly charged negative and positive ends, and therefore are more soluble in water, which is also polar.

NSOs may be present in fresh crude oils or fresh fuel-oil products; thus, these polar compounds could comprise part of the dissolved phase of a fresh crude or fresh refined product, depending on the pure-compound solubility and its mole-fraction within the mixture.

Important! Thus, the components of fuel likely to be found in the dissolved phase include:

- C6 to C11 mono-aromatics (BTEX and the alkylated benzenes)
- C10 to C14 PAHs (naphthalene, alkylated naphthalenes, acenaphthene, fluorene, phenanthrene, and anthracene)
- C6 and smaller aliphatics
- Polar blending agents/additives (such as MTBE or ethanol)

Concentration of the Dissolved Phase from Laboratory Studies

In addition to evaluating the constituents within the dissolved phase, the Shiu, et al. (1990) and Potter (1996) studies investigated the maximum aggregate concentration of the dissolved phase (or bulk effective solubility) of fresh crude oils and fresh products. Excluding additives such as MTBE, the maximum aggregate concentration of the dissolved phase of fresh products tested is shown in the following table.

Table 13-5: Maximum Aggregate Concentration of Dissolved Phase of Fresh Products

Product	Maximum Aggregate Concentration of Dissolved Phase (mg/L)	Source
Gasolines	100 +	Shiu, et al. 1990; Potter 1996
Diesels and Fuel Oils	3 – 5, 40	Shiu, et al. 1990; Potter 1996
Jet Fuels	15 – 65	Potter 1996
Bunker C	6	Shiu, et al. 1990
Fresh Crude Oils	10 – 58	Shiu, et al. 1990

Note that concentrations of “TPH” measured in groundwater samples frequently exceed these aggregate values. This is because either a non-dissolved component was included in the sample, or because dissolved non-hydrocarbon constituents are present in the groundwater sample.

With regard to concentrations of individual constituents in the dissolved phase, Zemo (2006) compiled data from up to nine laboratory partitioning studies which measured effective solubilities of BTEX from fresh gasoline, and from four laboratory studies which measured effective solubilities of BTEX from fresh diesel; the averages for each fuel were reported as follows:

Table 13-6: Average Measured Effective Solubility of BTEX from Fresh Gasoline and Fresh Diesel

Average Measured Effective Solubility (mg/L)		
	From fresh gasoline	**From fresh diesel**
Benzene	29	0.23
Toluene	36	0.58
Ethylbenzene	2.7	0.12
Xylenes	15	0.46
Source: Zemo (2006)		

The data clearly show that the effective solubilities of BTEX from fresh diesel sources are lower than those from fresh gasoline sources, because the mole-fractions of BTEX are much lower in diesel than in gasoline (see Zemo 2006 for a detailed discussion). Note that, for a weathered gasoline or diesel source, the effective solubilities will be even lower than for the fresh source because the mole-fraction of the BTEX (or other soluble or biodegradable constituents) is lower in the weathered source (discussed below).

Important! Concentrations of any constituent in groundwater which significantly exceed its effective solubility, given a specific source type (especially for ethylbenzene and xylenes), indicate that a non-dissolved component (e.g., LNAPL or petroleum-affected soil particles) is likely present in the groundwater sample.

Table 13-7 shows the calculated theoretical maximum effective solubility of the individual constituents and aliphatic / aromatic fractions of the "average" fresh gasoline and the "average" fresh diesel, using the mass fractions and chemical properties shown earlier. Note that the calculated average values for BTEX are higher than those average values actually measured in laboratory studies. This is likely due to differences in mass fractions among the products tested and "non-ideal" behavior of the constituents.

Table 13-7: Theoretical Maximum Effective Solubility and Maximum Vapor Concentration Associated with "Average" Fresh Gasoline and Diesel

Component	**Fresh Gasoline**			**Fresh Diesel**		
	Avg.Wt. %	**Max. Eff. Sol. (mg/L)**	**Max. Vapor Conc. (mg/m^3)**	**Avg. Wt. %**	**Max. Eff. Sol. (mg/L)**	**Max. Vapor Conc. (mg/m^3)**
Benzene	2.0	36	8,300	0.03	0.54	124
Toluene	8.1	43	12,000	0.2	1.1	308
Ethylbenzene	1.7	2.9	957	0.07	0.12	40
Xylenes	9	16	4,500	0.5	0.9	252
Naphthalene	0.25	0.08/0.28	1.6/5.6	0.26	0.08/0.29	1.6/6
n-Hexane	2.4	0.43	2,160	---	---	---
Subtotal	**23.7**	**98**	**27,920**	**1.1**	**2.96**	**730**
Aliphatics						
C5-C6	21	7.6	250,800	0	0	0
>C6-C8	22	1.2	60,000	0	0	0
>C8-C10	9	0.04	3,200	2	0.0086	688
>C10-C12	3	0.00096	115	7	0.0022	264
>C12-C16	0	0	0	35	2.8 E-04	145
>C16-C21	0	0	0	34	8.5 E-06	42
>C21-C32	0	0	0	0	0	0
Subtotal	**55**	**8.7**	**314,115**	**78**	**0.011**	**1,240**
Aromatics						
>C8-C10	13	8.5	4,080	0.43	0.279	134
>C10-C12	2.3	0.58	81	0.74	0.185	26
>C12-C16	0	0	0	8	0.464	24
>C16-C21	0	0	0	12	0.078	1
>C21-C32	0	0	0	0	0	0
Subtotal	**15.3**	**9.1**	**4,161**	**21**	**1.0**	**185**
Totals		***115.8***	***346,196***		***3.97***	***2,155***

Notes:

1. Wt % = weight percent; converted to mass fraction (MF) (by multiplying by 0.01) for calculations.
2. BTEX, naphthalene (N), *n*-hexane weight percent are average values from Potter and Simmons (TPHCWG Vol. 2) 1998.
3. TPH fraction weight percents are average values from Oregon DEQ (2003), but revised to include trimethylbenzenes in C8 – C10 aromatics fraction.
4. Max. Eff. Sol. = Maximum theoretical effective solubility, calculated using Raoult's Law and mass fraction ($S_{effi} = S_i \times MF$). Constituent/fraction solubilities shown on Table 13-6.
5. Max. Vapor Conc. = Maximum theoretical vapor concentration, calculated using effective solubility × Henry's Law Constant (dimensionless) × 1000 L/kg. Henry's Law Constant shown on Table 13-2.

Effects of LNAPL Weathering on the Dissolved Phase

The following discussion explains why weathered petroleum products are less soluble than fresh products in groundwater.

As a crude oil or petroleum product weathers in the subsurface, both the constituents and the concentrations of the dissolved phase associated with the weathered petroleum will change. As the original soluble constituents are leached out of the LNAPL or are biodegraded, their mole-fraction decreases within the remaining mixture, which further decreases their effective solubility and thus the concentration of each in the dissolved phase.

For Example. The theoretical maximum concentration of dissolved benzene in water in the presence of relatively fresh gasoline is about 18 mg/L, assuming that the benzene mole-fraction is 1% of the gasoline (1,780 mg/L × 0.01 = 17.8 mg/L). But if the gasoline is significantly weathered and the benzene mole-fraction is reduced to 0.1%, the theoretical maximum concentration of benzene in the dissolved phase of the weathered gasoline is about 1.8 mg/L.

Ultimately, the residual LNAPL becomes depleted of soluble constituents to the point where such constituents will no longer partition to the dissolved phase in measurable amounts. This was illustrated by Shiu, et al. (1990), when dramatic reductions in the measured aggregate dissolved phase concentration were evidenced after laboratory evaporative "weathering" of crude oils and products. Most aggregate dissolved-phase concentrations of the weathered crude oil or product were reduced to about 1 mg/L or less, regardless of the original dissolved-phase concentration associated with the fresh oil or product. Accordingly, aggregate concentrations of dissolved petroleum hydrocarbons in groundwater at sites affected by highly weathered petroleum would not be expected to exceed about 1 mg/L in most cases, and could be non-detectable if the petroleum were sufficiently weathered (Zemo and Foote 2003).

Chapter 13: Fate and Transport of Petroleum in the Subsurface

Migration of Dissolved-Phase Constituents

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Once LNAPL has come into contact with water and has partitioned individual constituents into the dissolved phase in accordance with their effective solubilities, those dissolved constituents will migrate. The dissolved-phase constituents in the vadose-zone pore water can migrate (or "leach") to the water table if enough pore water is present and the constituents don't biodegrade/attenuate fast enough. Beneath the water table, the dissolved-phase petroleum constituents migrate with groundwater at a rate controlled by advection, hydrodynamic dispersion, sorption, and biodegradation. *Advection* is the transport of dissolved constituents by groundwater movement and is, therefore, dependent on the hydraulic conductivity and hydraulic gradient. *Dispersion* is the spread of dissolved constituents predominantly in the direction of groundwater flow, but also laterally (or parallel) and vertically (or perpendicular) to the direction of groundwater flow. Dispersion will tend to lengthen the plume and dilute the overall concentrations of dissolved constituents within the plume.

Sorption is defined as the interaction of a chemical with a solid. Many parameters affect sorption, including solubility, polarity, ionic charge, pH, redox potential, and the organic carbon/water partition coefficient (Piwoni and Keeley 1990; EPA 1995b). The tendency to adsorb is different for each dissolved constituent, and is represented in transport equations by the soil-partitioning coefficient, K_d. Sorption also causes the constituent to move more slowly than the bulk flow of water (retarded velocity). In general, finer-grained soils with greater clay content (higher organic content or diffusion into clay lattices) retard the migration of dissolved hydrocarbons more than coarser-grained materials do.

Dissolved-phase constituents are also affected by biodegradation. Hydrocarbon constituents are relatively easily biodegraded; ethers (e.g., MTBE) are less easily biodegraded. Biodegradation is a very significant factor for hydrocarbon plumes; a detailed discussion is provided in the *Biodegradation* section below.

All of these factors contribute to the ultimate length and width of the plume, and its concentrations over time. The combination of these factors (degradation and dispersion) is known as *natural attenuation* (also discussed in the Remediation chapter.) Even at sites where no active remediation has occurred, the dissolved hydrocarbon plume will eventually stabilize due to natural attenuation. A plume that is "stable" is a contaminant mass that has expanded to its maximum extent: the distance from the release where attenuation exceeds migration.

Plume Extent and Concentration Studies at LUFT Sites

Four significant petroleum hydrocarbon multi-site plume studies were conducted in the 1990s (Rice, et al. 1995; Buscheck et al. 1996; Mace, et al. 1997; Groundwater Services, Inc. 1997). These four studies did not include MTBE. A study of plume characterization for 190 sites in Arizona was published in 2004 (Dahlen, et al. 2004), and a study of plume lengths at 500 UST sites in the Los Angeles area was published in 2004 (Shih, et al. 2004). These two studies included MTBE. Recently, a significant 48-site plume study was published that focused on benzene, MTBE, and TBA (Kamath, et al. 2012). This study is significant because it contains a large amount of data collected after 2004, when MTBE was banned in California.

A California study (by the Lawrence Livermore National Laboratory; Rice, et al. 1995) and 1997 Response to USEPA Comments (Rice, et al. 1997) included 271 sites and showed that plume lengths change slowly, while average plume concentrations decline more rapidly. Plumes stabilize at relatively short distances from the fuel-release site. The 1995 study found that 90% of benzene plumes were less than 260 feet long (at 10 µg/L). In the 1997 Response to Comments, 90% of the benzene plumes were less than 340 feet long (at 10 µg/L) and 90% of the benzene plumes were less than 380 feet long (at 1 µg/L). The study found that *hydrogeologic parameters have little relationship to plume length*, indicating that biodegradation processes were a significant factor in plume length and attenuation of the concentrations.

Buscheck, et al. (1996) studied plume lengths and concentration trends at 119 sites in northern California. They found that, at 91% of the sites, the BTEX concentrations were either decreasing or showed no trend. In a subset of 62 sites with adequate data to establish plume length, Buscheck,et al. found that 85% of the benzene plumes were less than 200 feet long (at “detection limit”).

A Texas study evaluated 217 sites and found that most benzene plumes (75%) are less than 250 feet long (at 10 µg/L) and have either stabilized or are decreasing in length and concentration. *The study found that benzene plume length cannot be predicted on the basis of either site hydrogeology or previous remediation activities* (Mace, et al. 1997).

The Florida Risk-Based Corrective Action (RBCA) Planning Study analyzed groundwater data from 117 sites in 33 counties. The median plume length of the sites was 90 feet, based on BTEX data. Fifty-one percent of the sites in the study were at that time or had previously been subject to groundwater remediation (Groundwater Services, Inc. 1997). Approximately 75% of the petroleum plumes from the studies were less than 200 feet in length and were in a stable or shrinking condition (API 1998).

A more recent study of plume characterization at LUFT sites in Arizona (Dahlen, et al. 2004) did not present data in a format where the overall percentiles of plume lengths could be tabulated. Importantly, this study found that only 16% of all the wells at 190 sites were hydraulically downgradient of the source zone, 60% of the sites had only one or two downgradient wells, and 30% of the sites had no downgradient wells. The study found that caution must be exercised when drawing conclusions about plume extent from large database analyses.

The Shih, et al. (2004) study at 500 UST sites in the Los Angeles area showed that the mean benzene plume length (at 5 µg/L) was 198 feet and that 90% of the benzene plumes were less than 350 feet long (at 5 µg/L).

The addition of ethanol (EtOH) to gasoline at about 10% by volume may increase the length of a benzene plume by as much as 40% to 70%, based on plume-length studies conducted in Kansas and Iowa (Ruiz-Aguilar, et al. 2003). These studies showed the mean and median plume lengths for benzene from the two plume types as follows:

Table 13-8: Benzene Plume Length Comparison

	Benzene Plume Length (feet)	
	Mean	**Median**
Regular gasoline	193	156
EtOH-blended gasoline	263	263

Source: Ruiz-Aguilar, et al. (2003)

The benzene plume length increases in EtOH-blended gasoline because the ethanol is preferentially biodegraded over the hydrocarbons, which depletes the oxygen available in the source area. Benzene biodegrades fastest under aerobic conditions; therefore, its slower degradation rate under anaerobic conditions allows the plume to extend slightly longer. The length of the toluene plumes was not as impacted by the ethanol, most likely because toluene biodegrades relatively quickly under anaerobic conditions (see *Biodegradation* section below).

Plumes of MTBE can be longer than hydrocarbon plumes due to MTBE’s high *effective solubility* in water, its mobility, and its lower natural biodegradation potential. Dissolved-phase MTBE plumes have been documented to be thousands of feet long, especially when conditions in the aquifer are neither aerobic nor methanogenic (Wilson 2003); but other plume studies have shown that MTBE plumes were only a few hundred feet long (Reisinger, et al. 2000). Shih, et al. (2004) showed that the MTBE plumes at 500 LUFT sites in the Los Angeles area had a mean length of 317 feet (at 5 µg/L) and that 90% of the plumes were less than 545 feet long (at 5 µg/L).

Kamath, et al. (2012) studied plume lengths and attenuation rates for benzene, MTBE, and TBA at 48 gasoline UST sites across the U.S.; 63% of the sites were in California. This study provides important new information regarding plume characteristics because it includes data from long-term monitoring before and after MTBE was banned. In summary, this study found that 95% of the benzene plumes, 90% of the MTBE plumes, and 68% of the TBA plumes were stable or decreasing in size. The lower relative % of stability for the TBA plumes reflects the temporary build-up of TBA as MTBE biodegrades, and the sequential attenuation of TBA thereafter. The study found that measured and estimated plume lengths were similar among all three constituents, and that the median first-order attenuation rates were similar among benzene, MTBE, and stabilized TBA plumes. For sites with stable plumes, the median % reduction in maximum concentration over the study period was similar among all three constituents. Details are provided in the table below. This study shows that, since the banning of MTBE in 2004, plume lengths and attenuation rates for benzene and MTBE have been similar, which updates the technical understanding of long-term plume behavior.

Table 13-9: Summary of Key Results from Kamath, et al. (2012)

	Benzene	**MTBE**	**TBA**
Stable or decreasing in size	95%	90%	68%
Measured and estimated plume lengths (feet)	(at 5 µg/L)	(at 10 µg/L)	(at 12 µg/L)
Adjusted median	171	140	235
90%	356	454	366
Median 1st order attenuation rate (1/yr)	-0.59	-0.63	-0.52
Stable plumes: Median % reduction in maximum concentration to date	92%	99%	88%

Determining Groundwater Transport and Plume Length

There are various analytical models in the public domain that can be used to estimate chemical transport time and plume lengths (e.g., EPA 2009). These tools may be useful to evaluate plume stability, natural attenuation, and remediation time frame.

Volatilization from LNAPL or the Dissolved Phase into Vapor and Vapor Migration

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Volatilization of petroleum hydrocarbons in the subsurface occurs via the volatilization of constituents that are in the dissolved phase (in pore water or groundwater), volatilization from LNAPL (either mobile or residual) directly, and volatilization from impacted soil.

The partitioning between the dissolved and vapor phases is governed by Henry's Law. The tendency of the individual constituent to "escape" from the water phase to the vapor phase is proportional to its concentration in water, where the "proportionality constant" is the individual chemical's dimensionless form of the Henry's Law Constant. This relationship assumes local equilibrium between water and air and is useful for estimating the potential for transport from water to air, and from vapor to water. For LNAPL, volatilization can also be described by the chemical's vapor pressure and Raoult's Law. The vapor pressure is a measure of the "escaping" tendency of individual constituents from the LNAPL mixture to the vapor phase. As with effective solubility, the volatilization of individual constituents from LNAPL is a function of the mole-fraction of the constituents within the mixture.

While both of these media (pore/groundwater and LNAPL) contribute volatiles to the vapor phase, it is usually assumed that, in the source region, all of the phases are in equilibrium with each other. In other words, the dissolved-phase concentrations already account for the chemical's mole fraction in the LNAPL. Therefore, for most chemicals, using either Henry's Law from pore water or Raoult's Law from LNAPL will yield the same concentration in vapor. Because of this, most *models* predict vapor-phase concentrations by first calculating the dissolved-phase concentration (using effective solubility due to mole fraction) and then using the chemical's Henry's Law Constant, multiplied by the dissolved-phase concentration, to predict the vapor-phase concentration that will be in equilibrium with the LNAPL.

For Example. If benzene were dissolving from an LNAPL with a 1% mass fraction of benzene, its theoretical effective solubility would be 17.8 mg/L, and its theoretical maximum concentration in soil vapor would be 4,100 mg/m^3 (Henry's Law Constant of 0.23).

Table 13-7, earlier in this chapter, shows the calculated theoretical maximum vapor concentrations for constituents and TPH fractions of the "average" fresh gasoline and the "average" fresh diesel, using the mass fractions and chemical properties shown earlier. As shown on the table, the vapor phase associated with gasoline LNAPL would be dominated by the aliphatic hydrocarbons, and not by the aromatic hydrocarbons. This is expected because of the relatively high mole-fractions and high Henry's Law Constant for the aliphatics. Conversely, the vapor phase associated with a dissolved groundwater plume would be dominated by the aromatics, because the aliphatics are not typically dissolved in the groundwater.

Further Reading.

The following publications, written by Dr. Blayne Hartman in the LUSTLine Bulletin, discuss physical properties of petroleum hydrocarbons:

Oh Henry (a constant). June 1998. LUSTLine Bulletin #29, pages 17-18.

The Great Escape (from the UST). September 1998. LUSTLine Bulletin #30, pages 18-20.

Which Compound Requires More Attorneys: MTBE or Benzene? March 1999. LUSTLine Bulletin #31, pages 15-17.

Some Enlightenment on Density. June 1999. LUSTLine Bulletin #32, pages 24-25.

Migration of Vapor-Phase Constituents

Once the individual constituents are in the vapor phase, they can continue to migrate in the vadose zone. Transport will occur through diffusion caused by concentration gradients: closer to the ground, surface advection becomes more important due to changes in temperature and/or barometric pressure. These changes may be induced inadvertently in basements of buildings, or intentionally at vapor-recovery wells. The greatest movement will take place in the most permeable materials (Bruce 1993). Diffusion can result in downward migration of vapors, which can potentially impact groundwater. The extent of migration of vapor-phase constituents is controlled by multiple natural attenuation processes, including biodegradation; a detailed discussion of the biodegradation of petroleum vapors is provided in the *Biodegradation* section below.

In arid and semi-arid environments, the vadose zone will contain relatively low moisture for most of the year, and there is limited opportunity for volatilized constituents to dissolve into the water phase. If the soil-moisture content in the vadose zone is high, however, then relatively soluble compounds such as ethanol and MTBE will tend not to stay in the vapor phase, but rather will stay in the soil moisture (Day 2001).

Chapter 13: Fate and Transport of Petroleum in the Subsurface

Biodegradation

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Petroleum hydrocarbons are naturally biodegraded (oxidized) under both aerobic and anaerobic conditions, as documented in the literature. The simplest, most water-soluble constituents are biodegraded first (e.g., BTEX and the small *n*-alkanes); the more complex molecular structures are biodegraded more slowly. Also note that, for LNAPL, biodegradation only occurs at the air/oil and oil/water interfaces of the LNAPL, not in the center of the LNAPL. Both the vadose zone and the shallow saturated zone can transform from aerobic conditions to anaerobic conditions at LUFT sites due to continuing biological activity. In most subsurface environments, both aerobic and anaerobic biodegradation of petroleum hydrocarbons can occur, often simultaneously, in different parts of the plume. Petroleum constituents are biodegraded in soil, in groundwater, and in soil vapor.

Review of Redox Reactions

Redox reactions are the energy basis for biodegradation. Redox reactions (the common name for oxidation-reduction reactions) are fundamentally a set of reactions explaining the transfer of electrons between compounds. *Oxidation* is the half-reaction that involves the loss of electrons, and *reduction* is the half-reaction involving the gain of electrons. These reactions are always paired: oxidation and reduction happen virtually simultaneously.

The important aspect of redox reactions with regard to biodegradation is that they release energy which can be used for microbial growth. The more energy released in a redox reaction, the faster the microorganisms utilizing that reaction can grow.

Redox reactions involving hydrocarbons can derive the most energy from using oxygen as the *oxidizing agent* (also known as the electron acceptor). Anaerobic processes (those using anything other than oxygen as the oxidizing agent) release less energy, although as long as the reaction produces some amount of energy, it is still possible for microorganisms to utilize that energy. It should be noted, however, that different organisms are capable of utilizing different oxidizing agents, to the extent that those organisms which degrade hydrocarbons by using oxygen as the oxidizing agent are different species from those using, for example, nitrate.

Aerobic Biodegradation

Aerobic biodegradation is the breakdown of petroleum constituents by microorganisms (bacteria) using oxygen as the electron acceptor. Aerobic bacteria are usually indigenous to areas of the subsurface containing oxygen: the unsaturated zone and, if there is oxygen dissolved in the groundwater, the saturated zone. A reduction in dissolved oxygen concentrations within an existing petroleum plume is a strong indication that indigenous bacteria are already established and actively biodegrading petroleum constituents via aerobic respiration. Reduction of oxygen molecules is one of the most energetically favorable of the redox reactions involved in petroleum degradation. In general, dissolved-oxygen concentrations will be lower than background dissolved oxygen concentrations in groundwater that contains hydrocarbons due to the aerobic biodegradation.

Subsurface environments can become devoid of oxygen, especially if high concentrations of hydrocarbons are present. When this is the case, the rate of aerobic biodegradation will typically be limited by oxygen supply rather than by microorganism concentration. In any event, biodegradation of petroleum constituents occurs in most subsurface environments without the addition of supplemental bacteria (Wiedemeier, et al. 1995).

Low-molecular-weight aromatic hydrocarbons such as BTEX are easily biodegraded at the concentrations found dissolved in groundwater. *N*-alkanes between C10 and C22 are the most readily biodegradable hydrocarbon constituents. The biodegradation (redox) reaction causes the formation of a primary or secondary alcohol, with oxidation continuing to aldehydes and fatty acids for primary reactions, and to ketones and esters for secondary reactions (these are short-lived intermediate metabolites). The ultimate by-products of aerobic respiration are carbon dioxide and water.

Anaerobic Biodegradation

Dissolved oxygen can be rapidly depleted by increased levels of microbial respiration after petroleum hydrocarbons enter the groundwater system, resulting in anaerobic conditions within the dissolved plume. Anaerobic microorganisms are normally indigenous to areas of the subsurface that are devoid of oxygen, usually the saturated zone and low-permeability areas of the unsaturated zone. Certain requirements must be met for anaerobic (also referred to as "anoxic") bacteria to degrade petroleum constituents. These include the absence of dissolved oxygen, the availability of carbon sources (e.g., BTEX), electron acceptors, essential nutrients, and the proper ranges of pH, temperature, salinity, and redox potential. When oxygen is absent, nitrate, sulfate, iron(III), and carbon dioxide can serve as terminal electron acceptors (reduction).

During anaerobic biodegradation, hydrocarbon compounds are first oxidized to phenols or organic acids (for the aromatics), or to alcohols or organic acids (for the aliphatics), then transformed to volatile fatty acids, which are finally metabolized to carbon dioxide, methane, and water. Depending upon the type of electron acceptor present (nitrate, iron(III), sulfate, or carbon dioxide), pH conditions, and redox potential, anaerobic biodegradation can occur via denitrification, iron(III) reduction, sulfate reduction, or methanogenesis. Environmental conditions and microbial competition will ultimately determine which processes dominate but, in a typical aquifer, denitrification typically occurs first, followed by iron(III) reduction, sulfate reduction, and finally methanogenesis (Wiedemeier, et al. 1995).

In summary, both aerobic and anaerobic biodegradation can occur at petroleum release sites. Both aerobic and anaerobic biodegradation involve the destruction of hydrocarbon molecules by sequential oxidation reactions, ultimately producing organic acids which are transformed to carbon dioxide and water. Intermediate steps can produce and subsequently destroy: organic acids and esters, alcohols, phenols (from aromatics), aldehydes, and ketones.

Biodegradation of Vapor-Phase Constituents

Research has shown that vapor-phase petroleum constituents (BTEX has been most studied) from subsurface sources are usually biodegraded to very low or non-detectable concentrations within a few feet of the ground surface due to aerobic biodegradation, except in the case of high-concentration sources very close to and directly beneath the basement or slab of a building (Abreu, et al. 2009; Davis, et al. 2009; McHugh, et al. 2010). USEPA released an Information Paper (EPA 2011) that focused on the growing body of literature documenting the significant bioattenuation of petroleum vapors in the vadose zone, and the difference between the natural attenuation of petroleum vapors and chlorinated solvent vapors.

Several modeling studies have evaluated the combined impact of oxygen demand and degradation rate on petroleum vapor attenuation (Parker 2003; Abreu and Johnson 2006; DeVaull 2007; Abreu, et al. 2009). The results from Abreu, et al. (2009) indicated that, for the conditions modeled, petroleum vapor attenuation was not oxygen-limited for vapor-source concentrations less than 10,000,000 micrograms per cubic meter ($\mu g/m^3$) (10 milligrams per liter [mg/L]). In the cases where degradation was not oxygen limited, the distance required between the building foundation and the dissolved petroleum source to ensure attenuation of high concentrations of petroleum constituents depended on the first-order degradation rate. When using the geometric mean biodegradation rate for aromatic hydrocarbons (0.79/hour), a separation distance between the source and the building of 1 m (3.28 feet [ft]) was sufficient to achieve 100x bioattenuation (i.e., a 100x increase in attenuation relative to the "no biodegradation" case), while a separation distance of 3 m (10 ft) resulted in 10,000x bioattenuation. When using the lower degradation rate (0.079/hour), a separation distance of 3 m (10 ft) was required to achieve 100x bioattenuation.

Modeling conducted by DeVaull (2007) indicates a similar range of bioattenuation. In this paper, DeVaull reports that the distance over which the concentration is reduced by 50% was on the order of 2.3 to 29 centimeters (cm) for benzene. The bioattenuation expected to occur over a distance of 3 m is at least 1000x (API 2009). These results are discussed in the publicly available BioVapor model (API 2009) based on DeVaull (2007). This model can be downloaded from the API web page at http://www.api.org/.

The McHugh, et al. 2010 study provided a compilation of data from published field studies that showed significant bioattenuation of petroleum vapors in the vadose zone in many different hydrogeologic settings.

The available scientific literature related to petroleum vapor fate and transport suggests that:

- A number of mechanisms facilitate the transport of oxygen below building foundations, resulting in aerobic conditions at many sites, and
- Aerobic vadose-zone petroleum hydrocarbon biodegradation occurs wherever sufficient oxygen is present, resulting in rapid attenuation of hydrocarbon vapors over very short distances.

Refer to Appendix C of this Manual for a more detailed discussion about the impact of the attenuation of petroleum vapors in assessing potential human health risk.

Methyl Tert Butyl Ether (MTBE)

There is strong evidence that MTBE and TBA also naturally degrade under a variety of conditions, although not as rapidly as the BTEX compounds. At many sites, MTBE and TBA degrade under aerobic conditions; however, biodegradation of MTBE and TBA has also been reported under methanogenic, denitrifying, sulfate-reducing, and iron-reducing conditions (ITRC 2005).

Polar Non-Hydrocarbons in Groundwater Resulting from Biodegradation of Petroleum

The metabolic by-products of petroleum biodegradation (e.g., alcohols, organic acids, phenols, aldehydes, ketones) have oxygen in their molecular structures and are therefore "polar" molecules, which are very soluble in water compared to the hydrocarbons (which are non-polar).

The use of EPA Method 8015 for extractable total petroleum hydrocarbons (TPH; TPHd/mo or DRO/ORO) without silica-gel cleanup (SGC) has illuminated the fact that polar non-hydrocarbon compounds are generally present in groundwater at petroleum release sites where biodegradation is active. The polar compounds ("polars") are measured in extractable TPH because they are extracted and quantified together with the hydrocarbons unless the sample extract is subject to a SGC to separate polars from hydrocarbons (Zemo and Foote 2003) (see the Laboratory Analysis and Methods chapter for a detailed discussion). Note that EPA Method 418.1 included a SGC to isolate the petroleum hydrocarbons, but when California transitioned to EPA Method 8015 in the early 1990s, the SGC was omitted. This resulted in the "improved" GC-FID method reverting back to a "total organics" measurement rather than a "petroleum hydrocarbon" measurement.

At the time of this writing, some in the regulatory community have been questioning whether these polars are likely to be less, equally, or more toxic than the most toxic petroleum constituents within the diesel range (C11 to C22 aromatics) and whether they may pose a threat to groundwater quality. The following paragraphs provide an assessment of their potential relative threat to the waters of the State based on data that are readily available at the time of this writing.

The polar compounds in groundwater at petroleum release sites are typically the by-products of biodegradation (polar metabolites or polars). Both aerobic and anaerobic biodegradation involve the destruction of hydrocarbon molecules by sequential oxidation reactions, ultimately producing organic acids which are transformed to carbon dioxide and water. Intermediate steps in the oxidation process can produce and subsequently destroy: organic acids and esters, alcohols, phenols (from aromatics), aldehydes, and ketones (e.g., Atlas 1981; Wiedemeier, et al. 1995; Barcelona, et al. 1995; Dragun 1998). All of these compounds contain oxygen, and therefore are "polar" in molecular structure. The biodegradation of petroleum has been extensively studied for many years, and intrinsic and enhanced biodegradation is a widely accepted remedial method for petroleum releases (e.g., EPA 1999).

The mixture of specific polar metabolites present in the groundwater at a site where intrinsic biodegradation of petroleum is occurring is expected to be transient (i.e., it changes over time and space) due to changing oxidation/reduction (redox) conditions within the groundwater. Where studied, the organic acids have been shown to range from about 30% to more than 50% of the total amount of dissolved organic carbon present in groundwater downgradient from the petroleum release (Eganhouse, et al. 1993; Cozzarelli, et al. 1994; Thorn and Aiken 1998). The polars will persist in anaerobic conditions, but they have also been shown to naturally attenuate to carbon dioxide and water once the groundwater is sufficiently oxygenated (Eganhouse, et al. 1993; Cozzarelli, et al. 1994; Cozzarelli, et al. 1995). Using GC-MS and two-dimensional gas chromatography (GCxGC-MS), Zemo et al. (2012) studied the polar metabolites in groundwater at five fuel terminal sites with biodegrading sources; the groundwater was generally anaerobic. This study found that the polars identified in groundwater in the source areas were organic acids, alcohols, and ketones in approximately equal proportions, with few phenols or aldehydes. In the downgradient areas, the polars identified in groundwater were primarily organic acids, with fewer alcohols, far fewer ketones, and very few phenols or aldehydes. This study documented the continued sequential oxidation and attenuation of the intermediate polar metabolites to organic acids.

Data from hundreds of sites in California, where TPH is analyzed by EPA Method 8015 DRO without SGC, *and therefore includes the polars*, provide insight into the environmental fate of the polars. Based on these data, the polars in groundwater naturally attenuate because the DRO concentrations become non-detectable within a few hundred feet of the source area. The polars exist in the vicinity of the LNAPL in the smear zone and downgradient typically for a few hundred feet, due to the anaerobic shadow caused by the intrinsic biodegradation. Polars also appear to be naturally limited in vertical extent. Available data also indicate that the polars do not persist in oxygenated surface water. For example, a study at the Port of Los Angeles showed that DRO (without SGC) was not detected in surface-water samples collected from the immediate vicinity of a weathered product sheen (AMEC 2008).

With respect to toxicity to human health, available information indicates that the mixture of polar metabolites likely to be present has low toxicity potential. Comparison of the reference doses (RfDs; from EPA 2010 RSLs) for the 23 available constituents within the five families of polar compounds potentially present in groundwater due to petroleum biodegradation indicates that the polar constituents are of lower toxicity than the C11 to C22 aromatic hydrocarbons (RfD of 0.03; from MADEP 2003), with the exception of alkylated phenols and one of the six ketones (2-hexanone) (if present). Alkylated phenols and 2-hexanone have equal or higher toxicity than the C11 to C22 aromatic hydrocarbons, but they were not detected using GC-MS at a reporting limit of 10 µg/L and were infrequently identified using GCxGC-MS (Zemo et al. 2012). Most of the other polar constituents potentially present are less toxic than the C11 to C22 aromatic hydrocarbons by factors of 5 to more than 100. Tiwary, et al. (2012) showed that the vast majority of the polar compounds actually identified in groundwater by Zemo et al. (2012) were in structural classes of "low" potential toxicity to humans, based on USEPA toxicity ranking schemes.

With respect to organoleptic properties, comparison of odor thresholds for weathered and unweathered dissolved phases of gasoline and fuel oil #2 indicates that the polar compounds likely have higher taste and odor thresholds than the petroleum hydrocarbons. Gibbons (1940) found that, after fewer than 20 days of weathering in an uncovered beaker, the odor of the water samples (which would consist largely of polar compounds after the weathering period) *decreased* by up to a factor of 10.

With respect to ecotoxicity, available information is summarized as follows (from Zemo & Associates 2010): The dissolved polar biodegradation by-products can be toxic to aquatic species in controlled laboratory tests; however, field data show that these polars naturally attenuate very quickly in surface water and therefore pose little actual risk to ecosystems (Wolfe, et al. 1996). The attenuation is most likely due to their very high solubility and more rapid biodegradation in the aerobic conditions of surface water or the hyporheic zone of sediments. Data from the Port of Los Angeles (AMEC 2008) and Point Molate on San Francisco Bay (Entrix and TetraTech 1999) showed that sediments through which groundwater containing polars theoretically discharged were not toxic to aquatic receptors. Data from Portland Harbor [Oregon] show that the polars (measured as DRO without SGC) were not detected (<150 µg/L) in sediment pore waters at a depth of 30 cm beneath the river bottom immediately adjacent to a petroleum terminal with discharging groundwater (Integral 2006).

Given the transient nature of polar compounds resulting from the biodegradation of petroleum, and the facts that

1) Available data show that these polars naturally attenuate because they are not persistent in sufficiently oxygenated groundwater or surface water, and
2) Other available evidence suggests that the mixture of polars potentially present in groundwater is likely less toxic and possibly less odorous than the C11 to C22 aromatic fraction of the petroleum hydrocarbons,

these polars are considered to pose a relatively low risk to groundwater quality.

At this time, there is no evidence that polar compounds resulting from biodegradation of petroleum are creating a significant threat or nuisance to the waters of the State. Therefore, it is recommended that the focus of the State's resources and cleanup goals at petroleum release sites in California be the petroleum hydrocarbon constituents, and not the polar metabolites of biodegradation.

Chapter 13: Fate and Transport of Petroleum in the Subsurface

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Further Reading.

Modeling Subsurface Petroleum Hydrocarbon Transport: http://www.epa.gov/athens/learn2model/

Chapter 14: Conceptual Site Model

September 2012

Scope of This Chapter

This chapter discusses the Conceptual Site Model (CSM) and the integral part it plays in evaluating risk and guiding decisions regarding the investigation and remediation of Leaking Underground Fuel Tank (LUFT) sites.

The following sections describe the definition and objectives, development, and components, and provide examples of a CSM.

Definition and Objectives of a CSM

The California State Water Resources Control Board (State Water Board) Low-Threat Underground Storage Tank (UST) Case Closure Policy (Case Closure Policy) defines the CSM as: "a fundamental element of a comprehensive site investigation. The CSM establishes the source and attributes of the unauthorized release, describes all affected media (including soil, groundwater, and soil vapor as appropriate), describes local geology, hydrogeology and other physical site characteristics that affect contaminant environmental transport and fate, and identifies all confirmed and potential receptors (including water supply wells, surface water bodies, structures and their inhabitants)."

A CSM is a representation of the characteristics of the site in diagrammatic or written form that shows the possible and confirmed relationships between the source(s) of contamination, pathways, and receptors. The supporting data and analyses used to develop the CSM can be contained in multiple reports submitted to the regulatory agency over a period of time.

The objectives of a CSM are:

- To convey an understanding of the origin, nature, and lateral and vertical extent of contamination.
- To identify potential contaminant fate-and-transport processes and pathways. See the Fate and Transport chapter for further details.
- To identify potential human and environmental receptors that may be impacted by contamination associated with the site.
- To guide site investigation activities and identify additional data needed (if any) to draw reasonable conclusions regarding the source(s), pathways, and receptors.
- To frame the evaluation of risk to human health, safety, and the environment posed by releases at a LUFT site.

These objectives emphasize the need for an approach where a CSM is developed early and is iteratively refined through the project life cycle. Each piece of data that is collected should serve to refine the CSM. The Interstate Technology & Regulatory Council (ITRC) Vapor Intrusion Pathway Guideline document (ITRC 2007) provides additional information on developing a CSM.

Overview of the CSM Process

An initial CSM should be developed prior to any investigative work at a LUFT site. The initial CSM begins with a general understanding of the environment in which the LUFT site is found and the sources of potential contaminants. From there, the CSM describes the potential ways in which the contaminants may migrate in the environment and the receptors that may ultimately be affected. The intent is to provide a general idea of conditions at the site and indicates what type of additional data, if any, may be needed to determine the degree of risk associated with the site.

To develop an initial CSM, readily available information about the site, the nature and quantity of the release, and preliminary information regarding the migration pathways and potential receptors are gathered. Data may also be collected from available sources concerning surrounding populations, such as ambient water quality, use and approximate locations of nearby wells, sub-surface soil conditions, locations of subsurface utilities, climatological conditions, and land use. LUFT sites on nearby properties can be a good source of information. If there are nearby LUFT sites, this information can often be readily obtained from the GeoTracker system via the Internet (see the GeoTracker chapter).

The initial CSM should be used to guide the site-assessment activities (see the Site Assessment chapter). Any part of the CSM with significant uncertainty should be investigated to gain a better understanding and to refine the CSM. For example, the potential migration pathways may need to be investigated to determine whether or not they may be complete.

As additional data are obtained through site investigation, the understanding of contaminant transport at a site is refined, and sometimes revised.

Role of CSM for Risk Evaluation and Corrective Action

Once environmental samples are collected and analytical data are available during site assessment (or other phases of work, such as verification sampling during remediation, or confirmation sampling after a remedial action), the data are usually compared to the State Water Board Resolution 2012-0016, Low-Threat UST Case Closure Policy (Case Closure Policy) criteria and/or a site specific risk assessment is performed on sites that do not meet this policy criteria. Details are provided in the Risk Evaluation and Risk Management chapter.

If the information gained during the site assessment and risk evaluation indicates that the site may pose a current or future threat to human health, safety, and/or the environment, remediation or other corrective actions may be performed to mitigate the adverse effects of the release. The CSM is used to support proposed corrective action and guide remediation decisions and to ensure that potential receptors' exposures are appropriately eliminated or mitigated. The Corrective Action Plan chapter discusses good practices to be used during mitigation measures, and the Remediation chapter discusses several common remedial technologies employed at LUFT sites.

Updating the CSM

As additional information becomes available during site investigation or the site conditions change because of remediation, implementation of engineering controls, or other physical changes, the CSM should be re-evaluated and updated to incorporate the new data and any new understanding of the site conditions.

Legal.

The Case Closure Policy states that all relevant site characteristics identified by the CSM shall be assessed and supported by data so that the nature, extent, and mobility of the release have been established to determine conformance with applicable criteria in the Policy. It also states that a CSM is required under the general criteria to qualify for low-threat closure.

Components of the CSM

The following subsections describe the following components of a CSM:

- Hydrogeologic Setting;
- Source;
- Contaminant Transport and Exposure Pathways; and
- Receptors.

Hydrogeologic Setting

The hydrogeology (geologic factors that affect groundwater flow) of a site generally controls contaminant migration. Gaining an understanding of the geologic setting will also help to determine the pathways of migration. Much of the geologic information for a LUFT site can be gathered from historical reports, state and federal environmental databases (including boring logs obtained from cases in the GeoTracker database), and electronic and paper files covering the site and adjacent properties from various federal, state, and local agencies. Geologic aspects to consider when conceptualizing the geology at a LUFT site include:

- Site topography.
- Regional and local geologic conditions, including key aquifer and aquitard units.
- Site-specific soil texture/lithology (e.g., identify the predominant types of soil at the site, such as clay, sand, gravel, fractured bedrock, sediments, etc.), stratigraphy, and structures (dipping strata, faults, etc.) that may affect contaminant transport.

An understanding of the regional hydrogeology is also important in developing the CSM, especially if groundwater could potentially become impacted or is already impacted. Hydrogeologic features to be considered when developing the CSM include:

- Depth to the water table and its seasonal and known historical fluctuation.
- Groundwater flow within the shallowest aquifer (gradient direction, hydraulic conductivity, flow velocity), vertical gradient and degree of interconnection between unconfined, semi-confined, and confined groundwater.
- Whether or not the source is beneath a low-permeability surface (such as asphalt or concrete).
- Designated beneficial uses of groundwater beneath the site.
- Location of proximal supply wells that may influence groundwater flow or be potential receptors.
- Location of nearby surface-water bodies (if any) and potential transport pathways to surface-water bodies.

Source

A “source” is/are the environmental medium/media containing elevated contaminant concentrations associated with a release. Some risk-based corrective action (RBCA) programs define the source to be the original cause of the contamination; however, it is possible that, by the time a site becomes a LUFT site, the original source has been eliminated and the current source of contamination is soil and/or groundwater. Items to consider when determining the source are included in the list below. Some of the specifics may be determined based on historical information; others will need to be determined during site assessment.

- The origin(s) of the release (e.g., a leaking UST, dispenser, product piping, and/or surface spill).
- The number of USTs, the capacity of the tanks (e.g., 12,000 gallons), the products stored, the date of installation, and the removal date(s) (if applicable).
- The location of historical and active USTs, dispensers, and product piping.
- Details about the specific release location(s) (e.g., spill locations, and time frame/dates if known).
- The type of fuel released and the constituents of concern (COCs) associated with the fuel. The Fate and Transport chapter of this Manual presents guidance on identifying potential COCs associated with fuel.
- The historical use of fuel additives (e.g., methyl tertiary butyl ether [MTBE] or other fuel oxygenates, lead, lead scavengers).
- The media that are impacted (e.g., soil, groundwater).
- Other potential sources such as surface spills, aboveground storage tank (AST) leakage, or pipeline leakage.

The information needed to define the source—to be obtained during the site assessment—includes the following:

- Lateral and vertical extent of:
  - light non-aqueous-phase liquid (LNAPL)
  - COCs in unsaturated-zone soil
  - COCs in saturated-zone soil and the smear zone
  - COCs in groundwater
- The distribution of the COCs in the impacted media.

After evaluating the information obtained during site characterization, the extent and magnitude of the contamination can be defined. This is not an exact science; usually some assumptions will need to be made. In these cases, it is important, from a risk-evaluation perspective, to be conservative.

Contaminant Transport and Exposure Pathways

Pathways are the mechanisms by which a receptor may contact the COCs at a site. Exposure pathways consist of: (1) a source of contaminants (as described previously), (2) contaminant transport or the physical migration of the contaminants, (3) a point of exposure where the receptor may come into contact with contaminants, and (4) an exposure route (such as ingestion or inhalation).

Contaminant Transport

The Fate and Transport chapter of this Manual provides guidance on the various phases of petroleum constituents and how they behave in the subsurface. This information is critical for evaluating migration pathways or indirect exposure pathways. Typical migration pathways for LUFT sites include:

- LNAPL migration from the source area through soil.
- Dissolved-phase migration of COCs in the groundwater zone.
- Vapor migration of COCs from soil, groundwater, or LNAPL.
- Migration of COCs with groundwater and discharging of COCs to surface water.

In the surface-water example, the receptors may include ecological receptors as well as human receptors.

Points of Exposure

A “point of exposure” is where a receptor comes into contact with contamination. The exposure point may, or may not, be at the same location as the source. Exposure points should include potential future uses of the land, including adjacent land if there is a potential for exposure to off-site receptors (e.g., groundwater containing LNAPL moving downgradient, or volatilization into a future residence). Some examples of points of exposure include:

- Surface soil
- Water faucet used for drinking water
- Air inside a residence or commercial/industrial building
- Outdoor (ambient) air (from volatilization from surface soil to air)

For ecological receptors, the exposure point may be surface water or sediment that has been impacted (or could become impacted) from the source.

Exposure Route

Exposure routes are the mechanisms by which receptors may come into contact with contamination. Exposure routes at LUFT sites include:

- Dermal contact with contaminated soil
- Ingestion of contaminated soil
- Inhalation of outdoor air impacted by volatile emissions
- Ingestion of contaminated groundwater
- Inhalation of vapors (in indoor air at a residence or commercial building) from contaminated soil, groundwater, or LNAPL
- Dermal contact with impacted surface water and/or sediments

While developing the CSM, each of the elements of a pathway should be considered and investigated as necessary. For example, if groundwater at the site is not potable and the COCs in groundwater are not expected to migrate and impact a current or future potable water source above established limits, then the groundwater migration pathway may be eliminated.

Receptors

A receptor is a human or other living organism with the potential to be exposed to and adversely affected by contaminants as a result of contact with contaminated media either at the source or along a contaminant migration pathway. Potential receptors at LUFT sites may include:

- Adults and children in a residential scenario
- Adults in an occupational scenario
- Adults in a construction/utility worker scenario
- Adults and children using groundwater that has been contaminated by a release at the site as a potable water supply
- Aquatic receptors such as fish and benthic invertebrates

"Sensitive" human receptors are not evaluated separately, because the California Environmental Protection Agency (Cal/EPA) and the United States Environmental Protection Agency (EPA) toxicity values used in risk evaluations already consider sensitive subgroups.

Terrestrial ecological receptors may not be a very common type of receptor, considering that LUFT sites are typically small, paved, and located in largely urban and/or otherwise disturbed environments. Significant impacts to ecological receptors are unlikely to occur in most cases. However, if the potential to impact sensitive habitats or nearby surface water exists, these receptors should be included in the CSM. Situations in which potential impacts to ecological receptors may warrant evaluation include cases in which impacted groundwater may migrate and discharge to nearby surface-water bodies and cases in which the LUFT site is located in areas where special-status ecological receptors may reside.

It is important to consider the current and reasonably likely future uses of the site and adjacent properties when identifying receptors. Local zoning and planning agencies can generally assist in these determinations. Determining conditional uses at the LUFT site and adjacent properties is important, because changes in use may require consideration of different receptors. For example, a light-industrial park being re-developed for residential living needs to be evaluated for both adults and children who may live on the property.

Receptor Identification

The types of potential receptors located on adjacent properties should be identified if they could come onto the site or be exposed to the chemicals at the site. The extent of the area where receptors should be identified will vary based on the exposure pathways, as well as the extent and type of contamination.

In order to identify whether receptors may be drinking potentially impacted groundwater, a survey of water-supply wells near the site may be conducted. (See the Fate and Transport chapter for more information on potential plume lengths.) This survey is generally based on reviewing Department of Water Resources (DWR) well records and asking local water district and applicable City and/or County staff if they are aware of any wells within the search radius. Areas with known multiple private wells nearby may require door-to-door contact of local residents to determine their source of water.

Information about water-supply wells can often be obtained from the well owner. Desired information includes:

- Current status of the well (operational or idle) and pumping rate.
- Purpose of the well, such as drinking water, irrigation, industrial, livestock, etc.
- Well construction details (i.e., the depth and length of the well screen and sand pack interval).

Example CSMs for LUFT Sites

Typical LUFT sites will have four basic exposure scenarios involving typical combinations of source media, transport pathways, exposure media, exposure routes, and receptors:

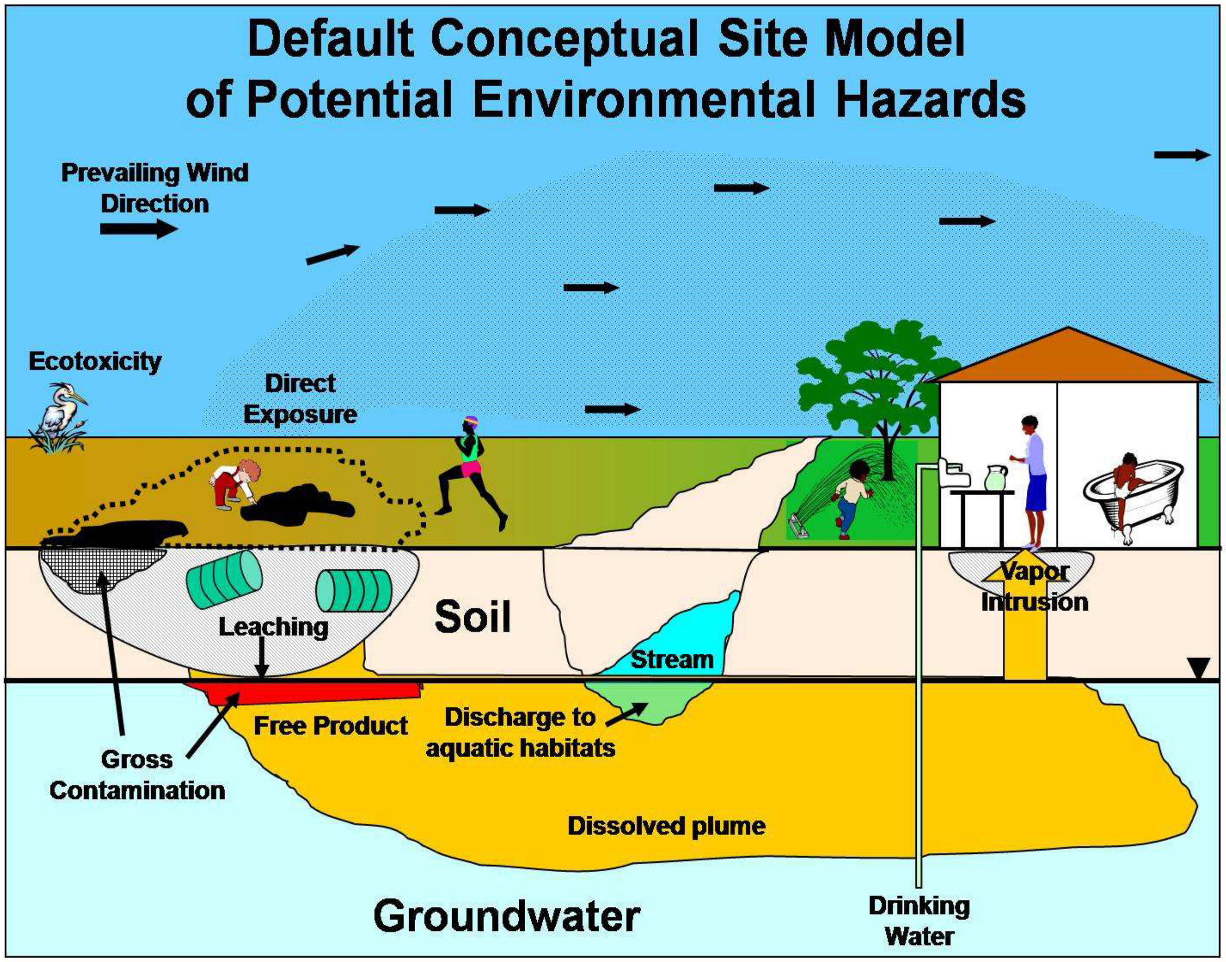
- Direct contact with soil (including ingestion, dermal contact, and inhalation of on-site emissions),
- Volatilization from impacted soil or groundwater into indoor air,

- Leaching from soil to groundwater and use of groundwater as a drinking-water supply,
- On-site groundwater that is already impacted above Water Quality Objectives (WQOs) moving downgradient and impacting groundwater offsite (and use of that water).

Note that other exposure scenarios, such as impacted groundwater migrating to surface water, may be important for a given situation and may need to be addressed; however, it is expected that the four scenarios discussed above will be the most commonly occurring scenarios for LUFT sites.

The CSM provided in the San Francisco Bay Regional Water Quality Control Board (Regional Water Board – S.F. Bay) Environmental Screening Level (ESL) document is shown in Figure 14-1 (Regional Water Board – S.F. Bay 2008), which is a good starting point when nothing is known about the site or the location and/or extent of contamination. This CSM shows the various exposure pathways and potential receptors that the ESLs can be used to address. One potential exposure pathway that is not shown on this figure is the migration of LNAPL or vapor contamination into conduits (or utility lines).

Figure 14-1: CSM from the San Francisco Bay Regional Water Board ESL Document



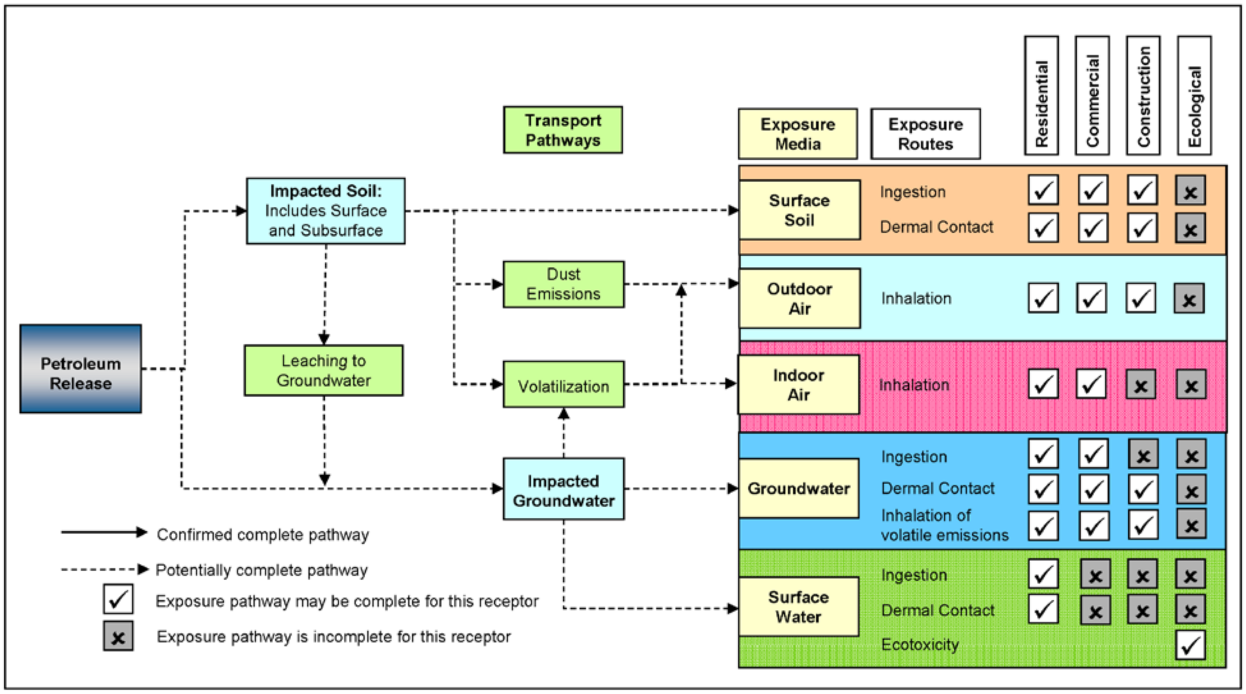
Note: This figure shows potential exposure pathways when little information exists about the site (Regional Water Board – S.F. Bay 2008). For most UST sites, a brief review of site information may eliminate potential exposures for ecotoxicity and for discharge to aquatic habitats.

The following examples discuss the evolution of a case and modification of a CSM including: (1) initial release has been identified, (2) after tank removal, (3) after the initial site investigation has been performed, and (4) for sites remaining in operation and potential future land use.

Initial CSM Example

Figure 14-2 shows an initial CSM for a former gas station where a release has been identified; however, no site characterization has occurred. The figure assumes that there may be surface-water bodies nearby and that impact to ecological receptors is possible, although highly unlikely. This is likely the situation at most service station sites, as they tend to exist in populated commercial areas, where ecological receptors aren't present. In this initial stage, all five exposure scenarios may be possible at the site and are therefore presented in the diagram.

Figure 14-2: Example of an Initial CSM When Site Characterization Has Not Occurred



Exposure Media	Exposure Routes	Residential	Commercial	Construction	Ecological
Surface Soil	Ingestion	✓	✓	✓	☒
	Dermal Contact	✓	✓	✓	☒
Outdoor Air	Inhalation	✓	✓	✓	☒
Indoor Air	Inhalation	✓	✓	☒	☒
Groundwater	Ingestion	✓	✓	☒	☒
	Dermal Contact	✓	✓	✓	☒
	Inhalation of volatile emissions	✓	✓	✓	☒
Surface Water	Ingestion	✓	☒	☒	☒
	Dermal Contact	✓	☒	☒	☒
	Ecotoxicity				✓

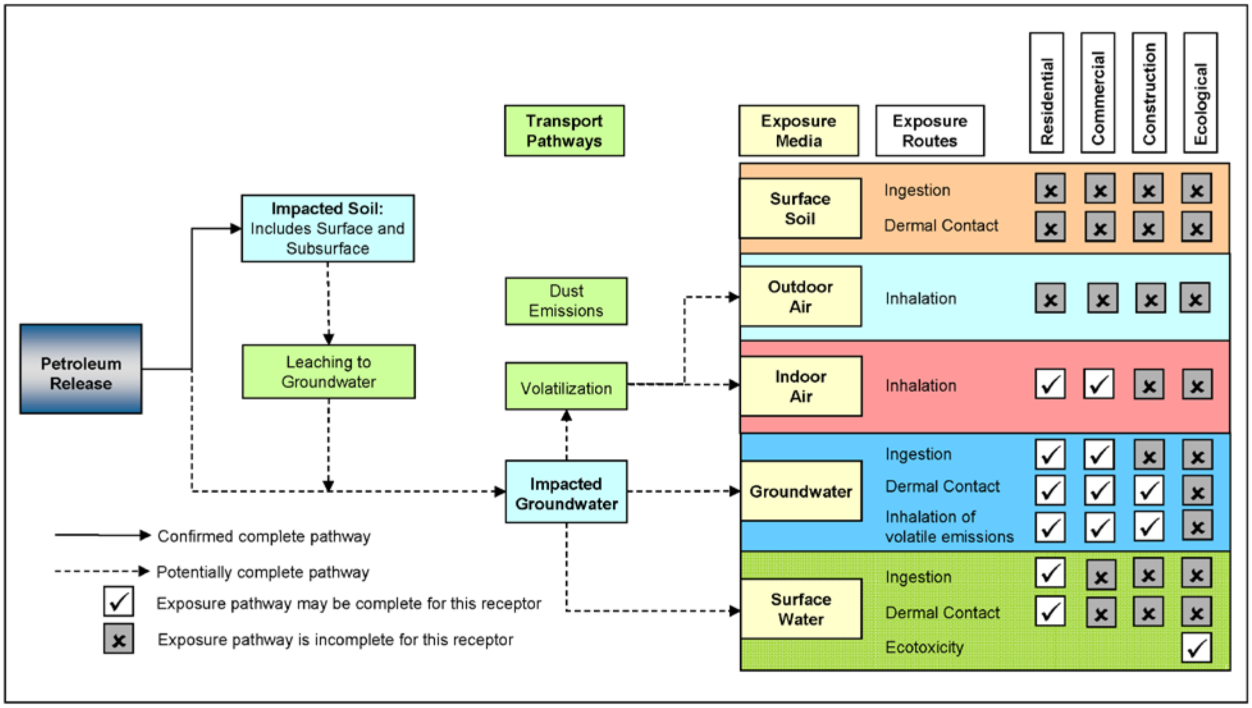
As data become available from source removal and site characterization, the CSM should be modified to reflect the current understanding of the conditions at the site.

CSM after Tank Removal Example

In this example, the tanks have been removed from the former gas station site. Petroleum hydrocarbon-impacted soil was not found until 10 feet below ground surface (bgs); however, the vertical depth and horizontal extent of the impacted soil and location of the water table are unknown. The site is located in a designated commercial/industrial area.

Because little information is known about the extent of the contamination and the hydrogeology of the site, the only pathways that can be eliminated at this point are those related to contact with surface soil. At this point, the CSM may be updated to look like Figure 14-3.

Figure 14-3: CSM Example – After Tank Removal and Observation of Impacted Soil in the Subsurface



Exposure Media	Exposure Routes	Residential	Commercial	Construction	Ecological
Surface Soil	Ingestion	☒	☒	☒	☒
	Dermal Contact	☒	☒	☒	☒
Outdoor Air	Inhalation	☒	☒	☒	☒
Indoor Air	Inhalation	☑	☑	☒	☒
Groundwater	Ingestion	☑	☑	☒	☒
	Dermal Contact	☑	☑	☑	☒
	Inhalation of volatile emissions	☑	☑	☑	☒
Surface Water	Ingestion	☑	☒	☒	☒
	Dermal Contact	☑	☒	☒	☒
	Ecotoxicity				☑

In Figure 14-3, the CSM has been updated after the depth to the contamination was determined to be more than 10 feet bgs. The CSM has been updated to remove the direct exposures such as dermal contact and ingestion of surface soil.

After Initial Site Investigation Example

After initial site investigation and collection of soil samples, the release was delineated both vertically and horizontally and the impacted soil was found to extend to groundwater, and LNAPL was discovered on the groundwater. This information does not change the CSM; therefore, the current CSM for this scenario is the one shown in Figure 14.3.

During risk evaluation, each of these potential pathways will be assessed in more detail and appropriate decisions will be made regarding additional investigation, cleanup, or monitoring of the site (see Risk Evaluation and Management chapter). For example, since the groundwater is already impacted by LNAPL, the contaminants in the unsaturated zone most likely will not increase human health risk from groundwater ingestion, unless there is mobile LNAPL still present (see Fate and Transport of Petroleum in the Subsurface chapter). Additionally, the volatilization-to-indoor-air pathway would need to be evaluated to determine whether the contaminated soil and/or groundwater is impacting receptors through the inhalation of volatile emissions and/or via ingestion or dermal contact with groundwater. Based on the evaluation, it may be determined that the soil and/or groundwater needs to be remediated.

Sites Remaining in Operation and Potential Future Land Use

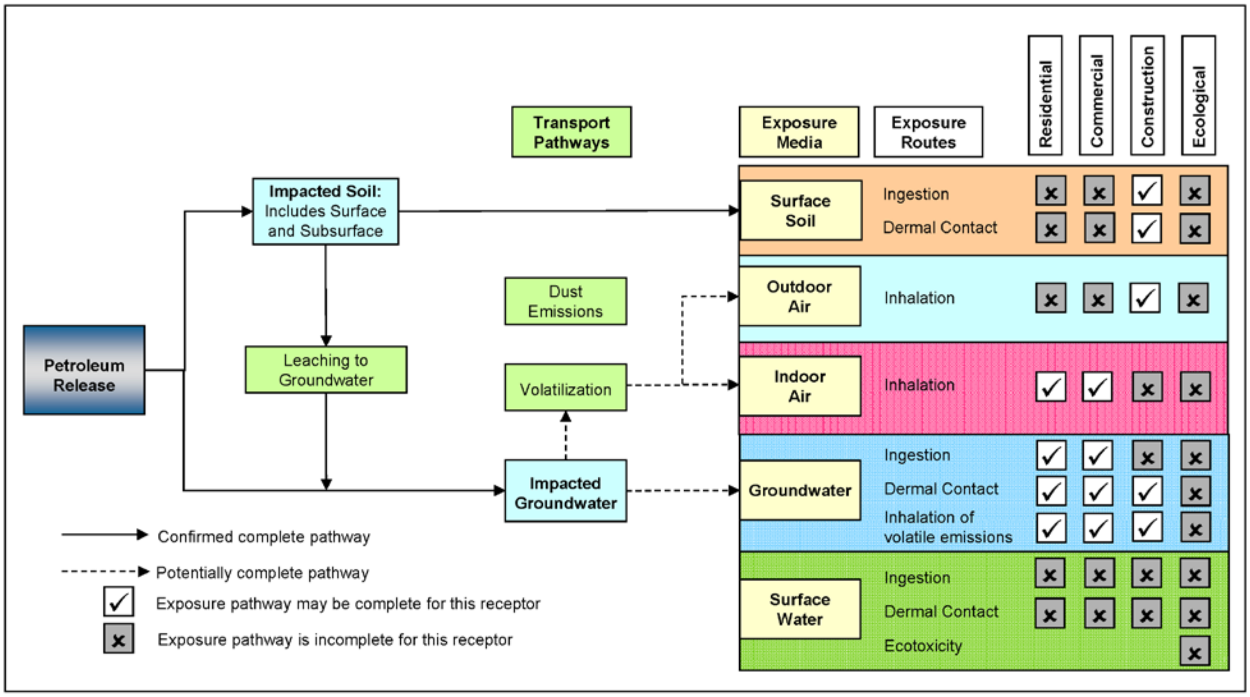
For a gas station that will continue to operate, impacted soil is usually covered with asphalt or concrete. This eliminates the potential for direct contact with soil and minimizes the potential for volatile emissions. If the soil concentrations are below mobility limits for the total petroleum hydrocarbon (TPH) mixture and the contamination has not reached groundwater (or the highest anticipated depth to groundwater), the potential for leaching to groundwater could possibly be eliminated if groundwater is currently not impacted because there is little to no infiltration (see Fate and Transport of Petroleum in the Subsurface chapter). Consideration should be given to whether the land use at this location could change, e.g., no longer contain an operating service station, and therefore the asphalt or concrete may be removed. In that case, direct contact with soil, inhalation of volatile emissions, and infiltration through the site may occur (irrigated landscaping or infiltration of rain water), leading to an increased probability of mobilizing residual contaminants. Also, for the operating service station (or any site), the potential to impact surface water should be considered.

Any trenching or construction work that would be performed while the station is operating will require that the construction workers have an adequate health and safety plan (HASP), and proper personal protective equipment (PPE) would be used to mitigate exposure to a construction worker. This exposure scenario does not need to be included in the CSM.

For operating sites where groundwater has been impacted above WQOs, potential impacts to private on-site water supply wells (if applicable) and off-site receptors may need to be evaluated for the groundwater ingestion pathway and volatilization of contaminants to indoor air. In this example, it is assumed that the groundwater is impacted; however, the plume is stable and is not discharging to surface water.

If the impacted groundwater is very shallow, and could be contacted while trenching or excavating offsite, then the dermal and inhalation of outdoor air pathways need to be included for the construction worker. In that case, the CSM will look somewhat like the diagram shown in Figure 14-4.

Figure 14-4: CSM Example – After Initial Site Investigation



Note that, in Figure 14.4, it is assumed that the groundwater has already been impacted. In this case, volatilization to indoor air and ingestion of groundwater remain as potential exposure pathways.

However, if no one on- or offsite is currently using the impacted groundwater, the groundwater ingestion pathway will not be complete. Consideration will need to be given as to whether WQOs will be met in the future before this groundwater could be used beneficially.

A gas station that is in the process of being redeveloped for a different land use, for example, a change from industrial to residential, must be evaluated consistent with the expected future land use. The re-evaluation will be at the discretion of the lead regulatory agency. In this case, direct contact with surface soils may be of concern, as well as any of the other three common exposure pathways. In this case, the CSM will look something like that shown in the initial CSM, when no data were available (Figure 14-2).

It is not within the scope of this document to cover the long-term management of the site. The lead regulatory agency decides when the site is ready for closure. Any conditions that are placed upon the closure are at the discretion of the lead regulatory agency.

References

Interstate Technology & Regulatory Council (ITRC). 2007. Vapor Intrusion Pathway: A Practical Guideline. VI-1. Washington, D.C.: Interstate Technology & Regulatory Council, Vapor Intrusion Team. January. More information at: http://www.itrcweb.org

San Francisco Bay Regional Water Quality Control Board (Regional Water Board – SF Bay). 2008. Screening For Environmental Concerns at Sites With Contaminated Soil and Groundwater. May. More information at: http://www.waterboards.ca.gov/sanfranciscobay/esl.shtml

California State Water Resources Control Board (State Water Board), Resolution 2012-006, Low-Threat UST Case Closure Policy. Adopted May 1, 2012, effective August 17, 2012.

Chapter 15: Site Assessment

September 2012

Scope of This Chapter

This chapter presents a summary of strategies, methodologies, and technologies used to assess releases at leaking underground fuel tank (LUFT) sites. Topics covered include strategies for assessment, pre-field work considerations, soil investigation, groundwater sampling, well construction and development, soil-vapor investigation, and a review of lessons learned from previous work.

Legal.

Title 23 of the *California Code of Regulations* (CCR) defines site assessment requirements (Division 3, Chapter 16, Article 11). Sample collection, management, and analysis should be performed in accordance with the procedures specified in:

- CCR Title 22, Division 4.5, Chapter 11, Article 3, Section 66261.20(c), and
- U.S. Environmental Protection Agency, Test Methods for Evaluating Soil Waste, Physical/Chemical Methods, SW-846, Third Edition (1986).

For the purposes of LUFT cleanup sites, site assessment is defined as the field activities necessary to assess the nature and extent of the petroleum release. Information obtained during the site assessment is used to update the conceptual site model (CSM), evaluate whether there are potential risks to human health and the environment, and identify appropriate risk-management activities (e.g., remediation or other control measures).

Note. State Water Board Resolution 2012-0016, Low-Threat UST Case Closure Policy (Case Closure Policy), contains several areas for which data must be generated during site assessment, and some reflect a new way of thinking about characterizing petroleum release sites. Therefore, it is important to consider the specific data requirements of the Case Closure Policy during development of the work plan/sampling plan. For example, characterization of shallow soil concentrations is required to evaluate both the vapor intrusion pathway and the direct contact pathway. This means that multiple soil samples must be collected and analyzed in the 0- to 5-foot depth interval (say, at 2.5 and 5 feet), and in the >5- to 10-foot depth interval (say, at 7.5 and 10 feet). This is a change in approach from typical historical practice, where soil samples were often collected only at 5-foot intervals starting at a depth of 5 feet. Also, the locations of nearby water supply wells (and their construction details, if available) need to be established with a high degree of certainty so that separation distance can be calculated once the downgradient extent of the groundwater plume is known.

Chapter 15: Site Assessment

Site Assessment Strategies

September 2012

Initial Approach to Site Assessment

The investigation approach can dramatically affect cleanup strategies, project costs, and schedule. Key parameters typically include pollutant distributions in soil, soil gas, and groundwater, their biodegradation rates, and their transport rates from the secondary source (source) toward potential receptors. Because investigators must extrapolate between borings and monitoring wells to estimate key parameters, and drilling mobilizations are major cost drivers, an *effective* investigation approach is critical.

Prior to any field activities, readily available information from nearby LUFT sites should be reviewed (e.g., GeoTracker). Information from other sites, such as drilling methods used, the depth to first groundwater, the lithology and depth of water-bearing units, direction of groundwater flow, and other issues (e.g., heaving sands) can be useful for planning site-assessment activities.

The following describes "step-out" *vs.* "step-in" sampling approaches, multiple phase *vs.* single phase investigations, radial sampling pattern *vs.* linear transects to delineate the areal extent of contamination, and screening methods.

"Step-out" *vs.* "Step-in"

A "step-out" site-assessment approach employs soil borings and monitoring wells at or near the source to estimate maximum pollutant concentrations, and "steps out" drilling locations away from the source to assess the extent of constituents of concern (COCs) along predicted pollutant transport directions. This approach, often the least expensive, is amenable to inactive sites with unlimited drilling access, but is not always practically feasible at active sites. For example, typical sources at active sites, such as fuel dispenser islands, piping, and USTs, are not safely accessible. Also, there are numerous sites which, despite the existence of monitoring wells, have data gaps; for example, unexplained discrepancies between apparent groundwater flow directions and pollutant distributions. In these cases, an investigator must often use a "step-in" approach.

A step-in strategy begins with borings and monitoring wells in areas with relatively low pollutant concentrations, and then investigates inward, toward the suspected source, along predicted permeability trends. For guidelines concerning where to begin a step-in approach, there is a discussion of typical plume length / extent in the Fate and Transport chapter. Decisions can then be made about the need for additional precautions to protect previously uncontaminated zones.

Note. Advancing borings in or near the source area may have unintended negative consequences. Drilling through either a confining layer or highly impacted soils can produce vertical conduits or drag contamination downward. In addition, drilling near USTs and piping increases the chances of encountering these underground objects during drilling and causing additional releases. Consequently, drilling in or near source areas should be undertaken with caution.

Multiple-Phase *vs.* Single-Phase Investigations

Prior to initiating field activities, it should be determined whether the work will occur in a single or in multiple phase(s). This decision is usually based on how quickly data gaps in the CSM need to be filled, the regulatory approval process, and the reimbursement approval process (for sites being reimbursed by the UST Cleanup Fund [Fund]).

In a multiple-phase investigation, the data are collected and evaluated in incremental steps. Further investigative work is determined by the data collected. Generally, as more information becomes available for a site, the site CSM is revised and used to plan the next phase of the investigation.

A single-phase investigation (also known as expedited site assessment) compresses the data-collection and CSM revision process into one mobilization of resources and equipment. Generally, this approach is used at sites that need a rapid turn-around time. While a single phase is faster, it may also be much more complex and require a dynamic work plan (discussed in the Work Plan chapter), *in-situ* data analysis, experienced personnel onsite with the discretion to make decisions regarding the field data and the scope of work, agreement on approach from all stakeholders, *and* a method for stakeholders to make decisions regarding in-field data.

Some pros and cons of multiple-phase and single-phase investigations are provided in Table 15-1.

Table 15-1: Pros and Cons of Multiple- and Single-Phase Investigations

	Pros	Cons
Multiple-Phase Investigation	• May allow for better planning by allowing for continuous update of the CSM and evaluation of data in incremental steps. • Allows for timely cost-management strategies to be developed. Long-term costs may decrease due to better management strategies. • May allow for early involvement of remediation engineers to evaluate data needed for assessment of remediation options. • May allow for better communication between lead agency and responsible party (RP)/consultants.	• Time requirements for site assessment may increase, thus increasing long-term disruptions to the site due to assessment activities. • Regular site operations and businesses may be affected over longer periods. • Potential development opportunities for the site may be delayed. • The potential for completion of exposure pathways to receptors increases due to lengthened site-assessment time. • Long-term costs could potentially increase due to more numerous mobilizations to site.
Single-Phase Investigation	• Site assessment may be completed more rapidly, potentially resulting in fewer long-term disruptions to the site. • Long-term site-assessment costs may decrease, due to lower numbers of mobilizations to the site and fewer long-term site disruptions. • Impacts may be remediated more rapidly, possibly minimizing potential for completion of pathways to receptors. • Site may be developed for new uses more rapidly.	• The possibility of incomplete planning increases due to unknown details about the site and an incomplete CSM, thus potentially increasing costs resulting from performing unnecessary work. • The planned field work may not provide a complete set of analytical data needed to fully characterize the site. • Incomplete data set may result in a multiple-phase investigation.

Areal Extent of Petroleum Hydrocarbons: Radial Sampling Pattern *vs.* Linear Transects

When determining the areal extent of contamination, it has been common practice to locate soil borings and monitoring wells at roughly equal distances from the source, stepping out until the edge of the plume is determined. This can work well at sites with inconsistent groundwater flow directions, complex permeability trends due to stratigraphy, and many obstacles such as buildings, utilities, etc.

At sites with relatively consistent groundwater flow directions along relevant permeable units, this radial pattern becomes elongated in one direction, and the resulting random spatial pattern complicates the analysis of the pollutant plume over time. A linear transect of wells perpendicular to the long axis of the plume allows a more consistent time series analysis (for example, a mass flux analysis).

Screening Methods

This section describes intrusive screening methods to collect general data that can be used to focus future investigations. Gross physical and chemical properties of the subsurface are collected to assess the approximate extent of contamination. General data are then used to efficiently design and select the sampling network, monitoring well design(s), and laboratory analyses that will be used to assess the nature and extent of contamination in more detail.

Typically, the screening tools are advanced into the subsurface with a drill rig using direct-push technology (DPT). Example screening tools include the Rapid Optical Screening Tool (ROST), Laser Induced Fluorescence (LIF), Membrane Inter Phase (MIP), electron acceptor mapping, soil-gas surveys, and soil headspace screening. To optimize the use of screening tools, work plans should provide for sufficient contingency borings to reduce overall project costs. Sufficient boring locations can help define source zones and guide investigations to define pollutant extent reasonably well in a single mobilization.

ROST, LIF, or MIP Coupled with CPT

Groundwater flow directions and plume extent are usually not known at the time of the first assessment. Screening technologies such as ROST, LIF, or MIP coupled with Cone Penetration Test (CPT) to define stratigraphy, locate separate-phase hydrocarbons, and minimize the potential for cross-contamination (a small-diameter hole that can be filled with bentonite slurry from total depth to surface) can be used. ROST, LIF, or MIP are useful for assessing source areas and the extent of separate-phase product, but are not used for assessing relatively low-concentration groundwater plumes, because the “detection” limits of these sensors are not low enough.

Electron Acceptor Mapping

Preliminary groundwater sampling for electron acceptors can also serve as a screening tool. For example, measurements of dissolved oxygen, carbon dioxide, methane, reduction potential (Eh), pH, iron II, sulfate, nitrate, and alkalinity, as well as petroleum analyses, can reveal zones of relatively slower, anaerobic, and/or faster, facultative and aerobic, bacterial pollutant decay. Investigators can construct preliminary maps of these parameters in the field to help select further drilling locations. See (for example) Chapelle, et al. 2000.

Soil-Vapor Investigations

Soil-vapor investigations can economically screen source-area locations and evaluate the relative size of an impacted area. Soil-vapor samples, both passive and active, can help delineate the extent of mobile chemicals in the vadose zone, and infer their distribution in underlying groundwater. Cost per sample is typically low relative to the cost of drilling deeper borings and installing monitoring wells.

After the soil-vapor evaluation phase is completed, soil borings or monitoring wells may be installed to further evaluate chemical impacts using the soil-vapor data as a guide.

Soil Headspace Screening

This field method can be used with soil samples to economically delineate the lateral and vertical extent of light nonaqueous-phase liquid (LNAPL) smear zones. The method is easy to perform (put soil samples into a zip-lock bag for a specified time period and then measure the volatized hydrocarbons in the bag using a photo-ionization detector [PID]), and provides real-time information in the field.

Background Sampling Strategy

Background samples are collected to investigate the naturally occurring or anthropogenic conditions that existed at a site prior to the unauthorized release. At most petroleum release sites, background concentrations are only established for heavy metals (i.e., cadmium, chromium, nickel, zinc and lead). However, background concentrations for petroleum hydrocarbons may need to be established where they are found to be naturally occurring (e.g., oil and gas fields). If other pollutant sources (e.g., other LUFT sites, dry cleaners, etc.) are within relevant distance, background groundwater samples can help to determine the relative contribution from the off-site source. GeoTracker and EnviroStor can be used to help locate nearby release sites.

“Additional Information” Sampling Strategy

Although sampling and analyzing for petroleum constituents in soil, groundwater, or soil vapor is the primary focus of site assessments, collecting additional data that are relevant for evaluating natural attenuation, fate-and-transport calculations, or design of active remediation systems should be considered at each stage of an investigation. These data are often not expensive to collect, and can help form a more accurate CSM. Such data include organic carbon content, density and other physical properties for soil, electron acceptors, general geochemical parameters, and oxidation-reduction (redox) conditions in groundwater.

Chapter 15: Site Assessment
Pre-Field Work Considerations

September 2012

There are several tasks to consider prior to beginning field work, such as preparing a work plan, acquiring appropriate permits, etc. The following is a discussion of important pre-field considerations. Please note that this is **not** intended to be all-inclusive, as each LUFT site is unique and has unique requirements. It is important for RPs and consultants to work with the regulatory agency overseeing the site assessment to ensure that pre-field considerations have been addressed prior to mobilization for field work.

Work Plan

Submittal of a work plan is required prior to conducting field activities associated with a LUFT site assessment, as discussed in the Work Plan chapter of this Manual.

Regulatory Requirements and Permits

It is important to identify the regulatory requirements prior to performing an investigation at a LUFT site. Regulatory permits may be required prior to site assessment (and cleanup phases). Contact the applicable regulatory agency (i.e., federal, state, county, and municipality) for details. This section describes typical regulatory permits that may be required for a LUFT investigation. Additional information may also be available in guidance documents provided by the regulatory agency.

The RP is required to obtain the proper permits in order to perform work. Permits may be required for ground disturbance activities such as advancing borings (including CPT points) and constructing and destroying monitoring wells. Depending on the location of the site, permits are typically obtained from either county or municipal agencies, such as environmental health/fire departments, water districts, planning departments, and/or building departments.

If work is being completed in public rights-of-way (sidewalks areas, roads, etc.), an encroachment permit is often required. If assessment is needed at an off-site location, or if the subject site is no longer owned by the RP, the RP (or RP’s agent) will likely need to obtain an access agreement with the owner(s) of the property where work is to be conducted.

As part of the well or boring permit process, many regulatory agencies require the property owner to sign forms indicating that the property owner agrees to have the assessment performed. If he or she refuses to grant reasonable access, the regulatory agency may require the property owner to conduct the required work at his/her own expense. This process can be very time-consuming, and should be factored into the schedule for work completion.

Regulatory Oversight

An inspector from the lead regulatory agency or local oversight agency which has issued a specific permit has the authority to be present during site work, unless prior approval to proceed without an inspector onsite has been obtained. Each agency may have its own specific notification requirements, including notification, or lack thereof, for routine monitoring or maintenance events. The agency has the regulatory authority to reject analytical or field results obtained during field work if the proper inspection arrangements have not been made and there is a reasonable suspicion that the data are not valid.

It is recommended, and may in fact be required by some regulatory agencies, that the RP and consultant contact the regulatory agency to schedule an inspection a minimum of three to five business days (or other agreed-upon interval among RP, consultant, and regulatory agency – the RP is responsible for confirming this interval) before proposed site work begins. If either the date or the field-work schedule is changed from a previously agreed-upon time, whichever party first becomes aware of the change notifies the other parties in the manner previously agreed upon (email, fax, etc.).

Utility Location and Clearance

California requires that the RP mark any underground subsurface work locations (e.g., drilling locations, excavation locations, trench locations, etc.) in white paint and contact Underground Service Alert North in northern California (http://digalert.org) or DigAlert in southern California (http://www.call811.com) at least 48 hours in advance of any work to acquire a ticket number. USA North/DigAlert will notify listed underground utility owners (members) with facilities near the investigative area. Members then send personnel to the site to locate the underground utility locations and/or clear the marked work locations within 24 inches of the marked location. USA can be contacted at (800) 227-2600 throughout California.

USA members are not responsible for clearing underground utility corridors on privately owned land. Consequently, the RP should review available as-built maps for underground utility locations. In addition, the RP should consider subcontracting a private and licensed underground utility locator for geophysical and intrusive methods for utility locating and clearance.

Important! The locations of underground utilities need to be identified before any drilling work or excavation work is performed at a LUFT site. Encountering underground utilities during drilling and excavation operations can be extremely dangerous, life-threatening, and costly.

Further Reading.

Further information on DigAlert and the law can be reviewed at www.digalert.org/index.asp, www.call811.com, or http://www.usanorth.org (for Northern California).

Geophysical Surveys for Utilities and Other Underground Features

Surface geophysical surveys are generally conducted to better understand the location of USTs and associated piping at LUFT sites, but may also be performed to investigate the location of drums, other utilities, building foundations, vaults, etc. Additionally, geophysical data can be used to identify former excavations. The primary intent of using geophysical data during site assessment is to gather as much information about subsurface objects and conditions as possible without disturbing the surface or conducting expensive exploratory excavation or trenching. Generally, available site as-built construction drawings and other documents should first be reviewed to evaluate UST and associated utility locations before conducting geophysical surveys. Geophysical surveys can be invaluable in directing site assessments; however, the accuracy of geophysical data is highly dependent on site conditions and the skill and experience of the geophysicist conducting the survey (EPA 1997, Department of Toxic Substances Control [DTSC] 1994).

Some of the geophysical survey methods used in site investigations are discussed below; Table 15-2 provides a list of pros and cons for each method.

- **Ground Penetrating Radar (GPR).** The process of transmitting electromagnetic energy into the ground and measuring the time it takes for that energy to be reflected back to the receiving unit. By measuring and logging the timing and strength of the returning signal, an image of the subsurface, including foreign objects, such as USTs, vaults, or piping, can be created.
- **Magnetic.** This method uses instruments called magnetometers, also known as magnetic locators, that measure variations in the earth's magnetic field caused by localized ferrous metals found in iron and steel pipes, valve and curb boxes (rebar), corner markers, wells casings, and steel drums and tanks. Magnetometers also detect the magnetic component of electromagnetic fields, and are therefore widely used to identify subsurface energized electric cables.
- **Electromagnetic Induction (EM).** EM is an advanced form of metal detection. By using an electric coil to create a magnetic field, the EM equipment can measure secondary magnetic fields created from buried ferrous metal objects, such as USTs and metal drums.
- **Line Tracing.** By inducing or impressing a signal into an exposed or known utility or piping (such as a metal water pipe or vent line), a receiver can be used to trace the subsurface location of the line. Additionally, non-

metallic lines, such as sewer pipes, can be traced by inserting a signal antenna connected to a transmitter into the length of the pipe and tracing it with the receiver. Line tracing is extremely valuable for health and safety during site-assessment activities, by identifying live utilities in drilling and excavation locations.

Intrusive Methods for Utility Location and Clearance

Minimally intrusive methods for utility clearance are typically performed as an extra measure of caution immediately prior to advancing soil borings. For UST or trench excavations, intrusive utility locating is performed prior to excavating and after a geophysical utility clearance survey, if performed. In areas where as-built drawings are unreliable or do not exist, and/or geophysical survey data are too cluttered or overloaded due to surface debris, subsurface metal, and/or magnetic soils, intrusive methods for locating utilities are recommended. It is recommended that the RP and/or the RP's agent(s) consider intrusive methods at the proposed drilling locations to a minimal depth of 5 feet below ground surface (bgs) before drilling operations begin. The law requires that the site be excavated to a point of "no conflict" 24 inches on either side of the underground utility/facility, so the exact locations can be known before using power equipment.

Some of the minimally intrusive methods used in site investigations are discussed below. Table 15-2 provides a list of pros and cons for each method.

- **Hand Excavation.** Excavate manually with hand-held, non-mechanical equipment, such as a hand auger or post-hole digger.
- **Excavation.** Excavate with a backhoe or similar piece of equipment.
- **Air or Water Excavation and Vacuum Extraction.** Excavation with air or water pressure to break up the soil and a vacuum device to collect the spoils. Vacuum extraction and excavation with pressurized air is also known as "air knifing."

> **Note.** An intrusive method for utility location and clearance is also known as "pot-holing." The term "pot-holing" comes from the practice of digging a series of holes to determine depth and direction of buried utilities and other obstructions. Any intrusive methods can be used for pot-holing.

Table 15-2: Pros and Cons of Utility Location and Clearance Methods

Geophysical Surveys (Non-Intrusive Methods)		
	Pros	**Cons**
GPR Imaging	• GPR data are relatively inexpensive to gather. • Gathering GPR data is non-destructive. • GPR can be used to identify metallic and non-metallic objects, as well as excavations. • GPR can be used on a multitude of sites with varying ground cover, including soil, asphalt, and concrete.	• GPR equipment is sensitive and can receive interference from structures, such as walls and ceilings, or from large equipment. • GPR may not be effective in collecting data below reinforced concrete. • Depending on subsurface soils, GPR may have a relatively low depth range. Moist clays restrict the GPR image depth more than dry sands do.
Magnetic	• Most common method used for initial utility clearance • Inexpensive, non-destructive, and fast	• Susceptible to false positives due to: 1. Magnetic mineralization of the subsurface soil 2. Non-utility-related ferrous metals 3. Aboveground electrical lines • Will not identify utilities housed in CPVC, PVC, or other non-ferrous material
EM	• EM data are relatively inexpensive to gather • Gathering EM data is non-destructive • EM can be used on a multitude of sites with varying ground cover, including soil, asphalt, and concrete • Good lateral resolution	• EM equipment is sensitive and can receive interference from vehicles, metal fences, metal structures, and reinforced concrete • EM will only identify metallic objects; it will not identify fiberglass or PVC • Poor vertical resolution
Line Tracing	• Line tracing data are relatively inexpensive to gather • Gathering line tracing data is non-destructive • Line tracing can be used on a multitude of sites with varying ground cover, including soil, asphalt, and concrete	• Line tracing usually requires a starting point. This can be an exposed utility or vent line, or a known subsurface utility location

Table 15-2: Pros and Cons of Utility Location and Clearance Methods (Continued)

Intrusive Methods		
	Pros	**Cons**
Manual Excavation	• Hand augering is relatively inexpensive • Equipment can be used in areas inaccessible to larger equipment (e.g., indoors and areas with overhead power lines)	• Labor intensive depending on soil type • Prohibitive in soil with large gravel, cobbles, construction debris, or hard rock • Requires sufficient PPE due to potential exposure to contaminated media
Excavation with a Backhoe	• Most common method for projects requiring excavation • Efficient means of excavation	• Potential to damage utilities and other obstructions; operator must use extreme care • Overhead power-line restrictions • Contaminated soil requires stockpiling and proper characterization and disposal • More area disturbed, buckets used in excavation are larger than hand tools • Requires ground crew in addition to the equipment operator
Hydro-Excavation and Vacuum Extraction	• Excavation is quick and safe	• Water required • Not recommended for areas with known contamination • Recovery, characterization, and proper disposal of water may be required • Use of water can mobilize contaminants and transport them further and deeper • Potential to damage utilities or other obstructions if high-pressure water streams are used
Air Knifing and Vacuum Extraction	• Quickly and safely excavate to determine location of utility or obstruction • Less potential to damage utilities than other means of excavation • Less expensive than using water for hydro-excavation • Automates pot-holing, less manual labor • No overhead power-line issues	• Potential access issues • Can impact soil-vapor samples, so adequate time is required between air knifing and soil-vapor sample collection

Chapter 15: Site Assessment
Soil Investigation

September 2012

A soil investigation at a LUFT site is conducted to characterize the source and the extent of a release. It also serves to establish the severity of the release and the impacts to receptors by providing concentrations of COCs. There are several methods available for investigating and collecting soil samples, as discussed in this section.

Laboratory Analysis and Methods

The laboratory analyses and methods for COCs in soil samples at LUFT sites are discussed in the Laboratory Analysis and Methods chapter of this Manual, which sets forth recommended testing for forensic purposes for soil and free-product samples.

Selecting the Proper Soil Investigation Method

A petroleum release can occur aboveground (spills and dispenser leaks) or in the subsurface (USTs and piping) at a LUFT site. In order to characterize the release and further develop the CSM, the area of impact needs to be evaluated using the appropriate investigation method.

Hand Auger

For shallow soil investigations (about 2 to 8 feet bgs or less), hand augering may be adequate. Soil samples can be collected using either a specialized bit or a hand-drive sampler loaded with brass tubes. Hand augers are also routinely used to clear drilling locations of underground obstructions.

Test Pit – Excavator

Test pits are frequently used to investigate shallow soil conditions and stratigraphy. The pit is usually dug using a backhoe or excavator; the size of the equipment used is dependent on the depth of the test pit. Test pits are particularly useful for obtaining a "bigger picture" cross-sectional view of stratigraphic contacts and the location of soil staining or the occurrence of LNAPL, as compared to borings. The sidewalls of test pits are usually logged by drawing a cross-sectional view and identifying:

- Soil types and the depth of contacts
- Observations of fill
- Observation of staining
- Important natural or man-made features
- The water table

Soil samples can be collected from test pits either by driving brass tubes into the sidewalls or bottom of the pit, or (in the case of deep pits) by driving a tube into the soil from the excavator bucket. Test pits are backfilled either with the excavated soil or imported fill in accordance with regulatory requirements. Compaction of the backfilled pit is also accomplished per regulatory requirements.

Drilling

There are several drilling technologies used to investigate the impacted area. Selecting the proper drilling method requires balancing all the objectives for the field work. Important criteria to consider include:

- Depth of the soil investigation
- Soil or rock type
- Sampling needs for soil and groundwater
- Access constraints

- Cross-contamination concerns
- Whether or not a groundwater monitoring well will be placed within the boring.

Consideration of the geology and hydrogeology at the site is important when selecting a drilling method. The depth to which the boring must be drilled to access the impact area and/or to install a well to monitor a selected water-bearing zone may exceed the practical depths of a particular drilling technique. In addition, certain saturated geologic materials, under high hydrostatic pressures, may either:

- Impose increased frictional resistance (i.e., expanding clays), which limits the practical depths reached by some drilling methods, or
- Create unstable borehole conditions (e.g., heaving sands), which may preclude the use of some drilling methods for installation of the monitoring well.

Chapter 15: Site Assessment
Soil Investigation: Drilling Methods

September 2012

The following is a discussion of various soil drilling methods. It is intended to provide insight as to when and under which conditions the method(s) could be implemented. The discussion describes methods typically used at LUFT sites; it is not intended to be a comprehensive description of drilling methods. There are ASTM standards or guides for many of these methods that can be consulted for more details.

Continuous Core *vs.* Discrete-Depth Sampling

The investigator must decide whether continuous core or multiple discrete-depth samples will be collected to evaluate site stratigraphy. Continuous logs of the subsurface are particularly valuable because they can be used to produce accurate hydrogeological cross-sections and help to develop a three-dimensional CSM.

Continuous cores can be collected with DPTs, hollow-stem augers (e.g., 5-foot split barrel), mud-rotary drilling (wireline system), or sonic drilling. It is recommended that continuous cores be collected at as many locations as necessary to characterize the site stratigraphy and the lateral and vertical distribution of petroleum at the site.

> **Important.** The historic practice of collecting soil samples for geological logging only at 5-foot intervals may result in an inadequate, incomplete, and often inaccurate understanding of site stratigraphy and migration pathways if qualified field personnel with experience in proper logging are not performing the field work. Because of this, the interval sampling approach is not recommended unless highly qualified and experienced soil and bedrock loggers who understand stratigraphy, especially depositional environments and California geology are onsite during sampling (see Soil Sampling/Logging section below in this chapter, and Appendix B.

Common Methods Used to Advance a Borehole

Various methods used to advance a borehole are discussed in subsequent sections; a summary table presenting some pros and cons of each of these methods is provided in Table 15-3; and Figure 15-1 presents some of the common drilling methods.

Whichever method is selected, great care must be taken when advancing borings or installing wells through LNAPL source zones. In these cases, special measures must be taken (e.g., conductor casing or “dual tube” methods) to reduce the potential for cross-contamination (drag-down) during borehole advancement and sampling.

Direct Push Technology (DPT)

DPTs, commonly used for preliminary investigations of LUFT sites, are a category of continuous-core equipment that drives steel rods into the ground using a combination of a hydraulic ram and a percussive hammer. Direct-push rigs (for example, Geoprobe®) are most commonly used for the collection of soil and grab groundwater samples. CPT and MIP rigs are also considered DPTs. DPTs allow cost-effective, rapid sampling and data collection in unconsolidated soils and sediments.

A variety of equipment is available, particularly in the type of attachments used at the end of rods to collect samples and data. Some examples of tools that can be deployed using DPT include:

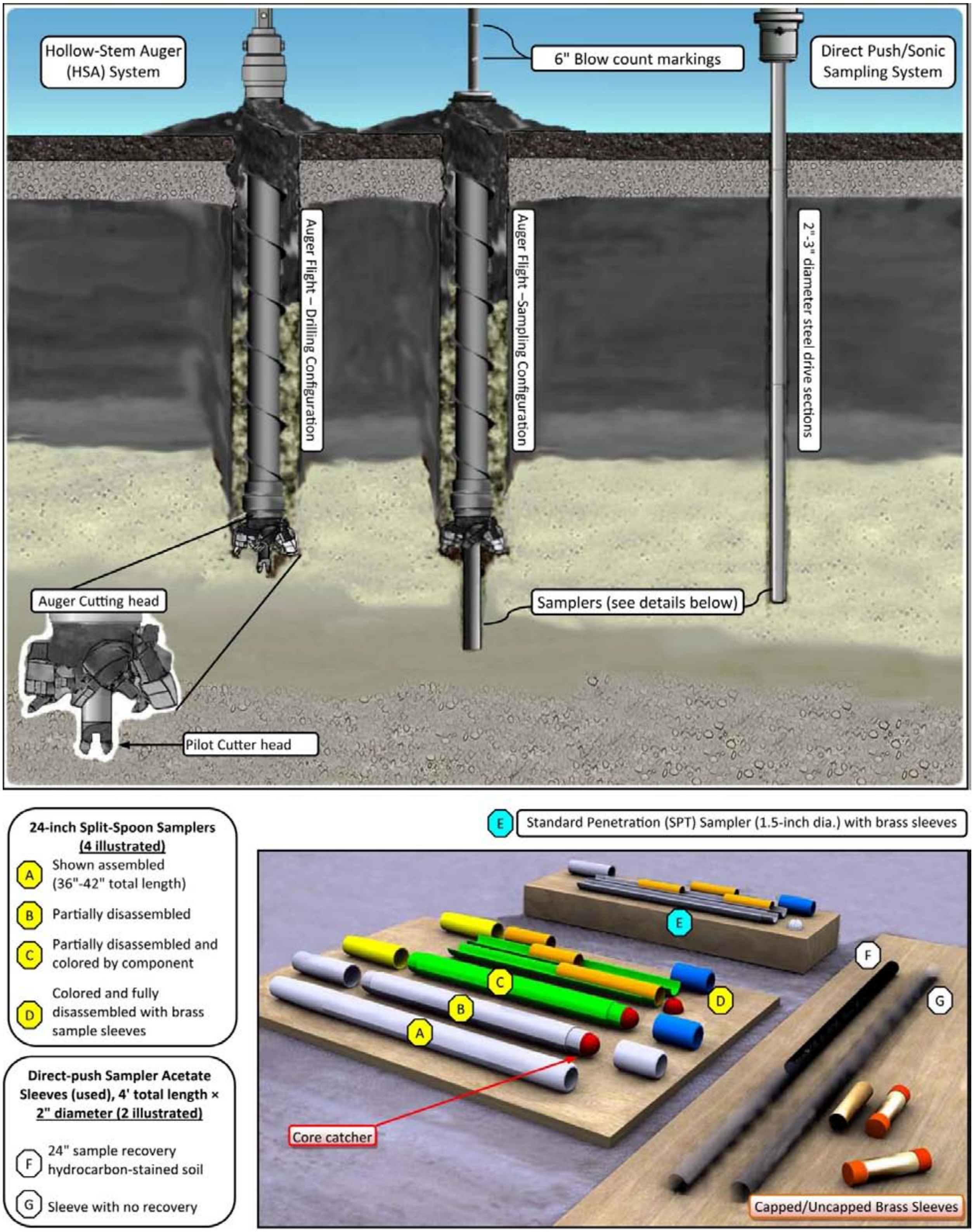
- Hydropunch-type samplers for collecting depth-discrete groundwater samples. (Discrete samples are those collected from a single distinct location.)
- Macrocores and large-bore samplers for collecting both continuous and depth-discrete soil samples.
- *In-situ*, direct-sensing instruments such as Cone Penetrometers and the MIP, ROST, and LIF tools.
- Soil-gas samplers.

These attachments can collect soil, soil-gas, or groundwater samples, perform *in-situ* analysis of contaminants, or collect geophysical data that are continuously logged as the DPT rods are advanced. As discussed above, the continuous logs of subsurface conditions provide particularly valuable on-site interpretation.

Direct-push rigs come in a variety of configurations, from truck-mounted systems to all-terrain track rigs and small dolly-mounted rams, and in single- and dual-tube configurations. In California, direct-push rigs can generally reach depths of 50 to 100 feet bgs in unconsolidated finer-grained soils, although CPT rigs may be able to reach 150 feet bgs in some conditions.

As a general rule, the larger and heavier the rig, the greater the depth it can achieve. For indoor work, small dolly-mounted rams can operate in small spaces, but need to be anchored to a concrete floor. In areas with cobbles, gravels, and hard-packed sediments, DPT is not a feasible option. The most appropriate uses of DPT are for shallow investigations in soft soil, for limited access (indoor) applications, and in sensitive areas to minimize surface disturbance.

Figure 15-1: Common Drilling Methods and Soil Sampling Systems



Hollow Stem Auger (HSA)

HSA is a drilling method commonly used at LUFT sites; it uses continuous-flight augers to penetrate the soil. As the augers are rotated, soil cuttings are brought to the ground surface via auger flights. A sampling barrel is often inserted inside the augers. Samples from discrete depths are collected by hammering a split-barrel sampler, typically 2 feet in length, into the native formation at selected depths. Alternatively, a 5-foot long split-barrel can be seated within the lead auger. A continuous core can be collected over numerous runs by advancing the sampler ahead of the auger. Each sampling method allows a minimally disturbed sample of native formation. Sample disturbance can be controlled by close evaluation of core recovery during drilling. A Standard Penetration Test (SPT) may also be performed using the split-barrel sampler to measure the geotechnical properties of soil. A variety of sampling tools can be used inside the hollow augers for soil and groundwater sampling and well construction.

Appropriate situations for HSA:

- Unconsolidated or partially consolidated lithologies, including gravels and cobbles.
- Maximum total depth capability up to 200 to 300 feet.
- Monitoring and/or remediation well installation.

Rotary Drilling Methods

Relatively less common at LUFT sites, rotary drilling is the process of advancing a borehole in which the ground is cut or crushed by a rotating drill bit. Rotary drilling uses circulating fluids (e.g., mud, water, or air) to remove the drill cuttings and maintain an open hole as drilling progresses. Although split-spoon samplers and coring equipment are available, rotary drilling is not generally amenable to extensive intact native formation sampling; boring logs are generally via monitoring of cuttings and, in some cases, follow-up borehole geophysics. Rotary drilling methods can be used to depths of several thousand feet. They are fast and effective in many types of lithology, but produce more waste for disposal. Rotary rigs are also very large, and can be highly disruptive to site activities. In addition, on a cost-per-foot basis, rotary rigs can cost several times as much as HSA rigs.

Air Rotary/Air Rotary Casing Hammer

Air rotary drilling forces air down the drill pipe and back up the borehole to remove the cuttings. If borehole stability or cross-contamination is a concern, then air rotary casing hammer (ARCH) can be used. ARCH is a drilling technique in which a hollow casing is driven at the same time the borehole is advanced by the rotary bit. The casing, which surrounds the drill pipe, is driven into the formation using a hammer which pounds the casing into the formation with a number of successive blows. This process seals off the borehole and minimizes cross-contamination.

Mud Rotary

Mud rotary drilling forces drilling mud, a water-based drilling fluid, into the drill pipe and through the bit. The drilling fluid/mud is used to lubricate and cool the drilling bit, stabilize the borehole, and carry drill cuttings to the surface. When the drill cuttings are carried by the mud to the surface, they settle out of the mud in a settling pit. The mud is then re-circulated back into the borehole. Additional mud is added as the well gets deeper and mud is lost to the formation(s) being drilled (Nielsen 2006).

Assuming that the mud is carefully monitored and a proper filter cake or mud cake is developed along the borehole wall, the mud rotary drilling method can reduce the potential for cross-contamination through an aquifer to a deeper zone. Like air rotary, mud rotary is costly as compared with HSA drilling, causes business and traffic flow disruption at typical LUFT sites, and is therefore seldom used. Although use of a mud rotary rig helps prevent cross-contamination when drilling through shallower parts of the saturated zone to a desired deeper location, other more cost-effective and less disruptive methods can be used to achieve the same goals.

For Example, use of conductor casing or a large-diameter auger flight to seal the borehole while installing a monitoring well at a particular depth interval is just as effective, and far less costly, than using a mud rotary drill rig.

Sonic Drilling

Also relatively uncommon at typical LUFT sites, sonic drill rigs use an oscillator to produce high-frequency vibrations in the sonic rig drilling bit, which vibrates vertically as the bit and casing assembly is rotated downward. The vibrations fluidize softer materials, and create fractures in hard soils and/or bedrock formations. The vibration frequency can be altered by the driller to adjust to different circumstances.

Sonic drilling is less cost-effective for shallow borings (less than 50 feet) because of the time and consequent cost of setup at each boring. Sonic drilling should be considered in situations where HSAs have difficulty, such as hard soils with gravels and cobbles or bedrock, deep drilling, and in instances where the shallow water-bearing zone should be isolated while the well is being installed in a deeper zone.

Table 15-3: Pros and Cons of Various Drilling Methods

	Pros	Cons
DPTs	• Reduced surface disturbance. • Minimal waste generation. • Small footprint for limited-access work. • Large variety of limited-access equipment options as compared with HSA. • Ideal for Hydropunch-type groundwater sampling. • Small-borehole diameter well suited for soil-gas vapor well construction. • Small-diameter wells can be installed using pre-pack well screens. • Ideal for one-time chemical injection points. • CPT rigs with ROST, LIF, or MIP capability generate a detailed lithologic and separate-phase product log in real time without producing soil waste.	• Usually limited to drilling and shallow soil sample recovery in unconsolidated soil materials and very soft rock. Cannot penetrate most bedrock. • Difficult to impossible to penetrate cobbles, gravels, or hard-packed soil. • May yield inconsistent core recovery. • Single tube has higher risk of cross-contamination. • Dual tube can decrease core recovery and consistency. • Cannot be used to collect many geotechnical samples. • Borings cannot be converted to conventionally sized (2-inch diameter or greater) monitoring and/or remediation wells. • CPT, MIP, and LIF data need to be confirmed by actual site data collected by traditional methods. • ROST, LIF, and MIP not typically sensitive enough to screen for relatively low-concentration dissolved-phase plumes. • Proprietary soil gas samplers specifically designed to be used in a Direct Push boring do not consistently produce representative samples.

Table 15-3: Pros and Cons of Various Drilling Methods (Continued)

	Pros	Cons
HSA	• Suitable for most exploratory boring and well-installation situations. • Ideal for collection of geotechnical samples. • Numerous soil sample tools of various diameters and lengths are available. • Cases upper part of boring to prevent caving and minimize cross-contamination. • Relatively quick and effective in poorly consolidated formations. • Does not introduce drilling fluids into the borehole. • Can install well screen, casing, and annular materials during auger removal. • Larger-diameter augers can be used as temporary casing for the installation of second, deeper-zone monitoring wells. • Larger diameter allows more options for collecting grab groundwater samples .	• Large surface disturbance as compared with DPT. • Greater waste generation as compared with DPT. • Fewer limited-access options than with DPT. • Limited diameter range for borings. • Not appropriate for bedrock drilling. • Large diameter borings poorly suited for soil-gas vapor well construction. • Difficulties caused by loose or flowing sands. • Smearing of clays may seal off water-bearing zone.
Air Rotary/ ARCH	• Can drill to great depths and through very hard materials such as bedrock. • Provides temporary casing to minimize cross-contamination and establish borehole stability for well construction (ARCH technique). • Does not introduce drilling fluid into borehole. • Provides identification of most water-bearing zones. • Can collect drive soil samples (ARCH technique).	• Seldom needed for most LUFT sites • Cannot collect continuous core and samples occur as small particles that are difficult to interpret. • Air used in the drilling process can strip volatile organic compounds (VOCs) from the soils and groundwater, negating any value from sampling. • Large rigs can cause disruption to business, traffic flow at typical urban gas station settings; safety issues; air compressor and casing hammer are very noisy. • Not cost-effective compared with HSA rigs; use only if too deep or too hard for HSA.

Table 15-3: Pros and Cons of Various Drilling Methods (Continued)

	Pros	Cons
Mud Rotary	• Capable of deep drilling (>1,000 feet). • Capable of penetrating bedrock. • Capable of continuous coring using wireline system.	• Well development (described later) is more problematic, since the mud needs to be removed. • Cannot discern the depth of the water table during drilling. • Costly compared with HSA drilling, even compared with conductor casing installed while using HSA. • Used drilling mud must be managed as a waste. • Large rigs and support equipment are disruptive to business and traffic flow at typical LUFT location and also pose a safety hazard.
Sonic Drilling	• No drilling fluid required. • Can drill through bedrock or cobbles. • Casing installed in boring during drilling, so no caving likely. • Capable of deep drilling (>1,000 feet). • Continuous core collected in every boring. • Safe and rapid method. • Limited waste generated (very low quantity of drill cuttings). • Comparable in effectiveness to conductor casing in sealing shallower parts of the water-bearing zone while installing deeper monitoring wells. • Newer rigs come in a variety of sizes.	• Causes subsurface temperature to increase slightly; may cause some volatilization of contaminants. • Higher cost than HSA rig on a per-foot basis. • Rigs can be larger than many HSAs (but smaller than most rotary rigs).

Common Drilling Problems

Drilling refusal and heaving sands are two common issues encountered when drilling in the subsurface, as discussed below.

Drilling Refusal

Drilling refusal occurs when the drill bit or split-spoon hammer cannot penetrate to the desired depth. This is usually because the material is too hard for the rig or method used. If refusal is encountered, the options are:

- Evaluate the data collected in terms of assessment goals, and confer with the regulator to determine whether sufficient information has been obtained such that, even though refusal has been met, no additional drilling is required.
- If refusal is met before sufficient information has been obtained to meet agency requirements, remobilization with another type of rig may be necessary.

Heaving Sands

Heaving sands occur when the drill bit penetrates permeable, unconsolidated, and saturated sand that has sufficient hydraulic head to cause pressurized wet sands to “heave” up inside the auger, preventing the well from being set at the depth drilled.

There are several methods for counteracting heaving sands. It is recommended that, prior to starting drilling, local drillers and the lead regulatory agency be consulted to determine whether the site may have heaving sands and what methods for installation of wells have been used successfully. There are several techniques used to maintain a positive pressure head within the auger column; most include pumping clean water (as drilling fluid) into the auger column. One solution is to re-drill to the desired depth, using a wooden plug in the bottom of the auger. The wooden plug can be knocked out of the bottom with the split spoon when the well is ready to be set. The driller will have to work quickly to place the casing at the correct depth before the sands flow back in through the bottom of the auger. Alternatively, sonic- or mud-rotary drilling methods can be used, but these are more expensive than HSA drilling.

Chapter 15: Site Assessment
Soil Investigation: Soil Sampling and Description

September 2012

The Low-Threat UST Case Closure Policy (Case Closure Policy) requires characterization of soil concentrations within the upper 10 feet of the surface for evaluation of both the vapor intrusion pathway and the direct contact pathway. To evaluate a site against the Case Closure Policy, multiple soil samples should be collected and analyzed within the 0 to 5-foot depth interval (e.g., at 2.5 and 5 feet bgs), and between the 5 to 10-foot depth interval (e.g., at 7.5 and 10 feet bgs). This is a change in approach from typical historical practice, where soil samples at LUFT sites were often collected only at 5-foot intervals starting at a depth of 5 feet bgs.

Soil–Sample Collection Methods

There are many guidance documents regarding the proper collection of soil samples for chemical analysis. Standard soil sample collection procedures are discussed in 1) *EPA 1992 Guidance: Preparation of Soil Sampling Protocols: Sampling Techniques and Strategies (this document also has a comprehensive treatment of sampling statistics) (EPA 1992); 2) EPA Region 4 and the Science and Ecosystem Support Division (SESD) 2007 Operating Procedure, Soil Sampling (EPA 2007); and 3) EPA Region 9 Laboratory 1999 Guidance: Field Sampling Guidance Document #1205, Soil Sampling (EPA 1999). It is important for the RP, the consultant, and the lead regulatory agency to agree on proper sampling protocols.*

Typical practice has been that soil samples for chemical analysis are collected in sleeves or liners that line the sampling barrel (e.g., acetate sleeves for DPT and brass sleeves for split-barrel samplers). At the desired sampling depth, the DPT sleeve is cut and capped, or the brass sleeve is selected and capped. It is also possible to collect a soil sample for chemical analysis from an unlined sampling barrel by quickly driving a brass sleeve into the soil core and then capping the sleeve.

The implementation of EPA Method 5035 for preservation of soils collected for analysis of volatiles (e.g., total petroleum hydrocarbons as gasoline/ gasoline range organics [TPHg/GRO] or volatile organic carbon [VOCs]) has necessitated slightly different soil-sampling methods than did historical protocols (DTSC 2004). Method 5035 is a preparation method for soil samples that minimizes the loss of volatiles and is the preferred preparation method for California. More details on the method can be found at www.epa.gov/osw/hazard/testmethods/sw846/pdfs/5035.pdf. The sample to be analyzed for volatiles is collected by removing the top 1 inch of soil from the sleeve, collecting the sample into the EPA Method 5035 preservation apparatus, and chilling as required. For samples to be analyzed for semi-volatiles (e.g., total petroleum hydrocarbons as diesel / diesel range organics [TPHd/DRO] or polycyclic aromatic hydrocarbons [PAHs]) or metals, the sleeve is sealed at both ends with Teflon™ film, capped, and taped using non-VOC containing tape. In all cases, samples are labeled and placed on ice in a cooler under chain-of-custody for transport to a State-certified laboratory for analysis. Samples should be delivered to the laboratory within 24 to 48 hours of collection, if possible, to limit the potential for analysis outside of method holding times.

For non-DPT methods, samples for soil description are typically collected using a split-barrel sampler that is not lined with sleeves. The barrel is opened and the soil is visually examined and described (discussed in detail later). Soil samples from DPT are described after cutting open the acetate sleeve. In all cases, the entire soil core can be screened using a PID to evaluate whether petroleum impacts are present. Soil from selected depths can be subjected to headspace screening, where soil is placed in a sealable plastic bag (e.g., Zip-Lock® bag) for an appropriate amount of time to allow volatilized constituents to enter the headspace.

Note. Samples are not to be sealed with duct or electrical tape, as the adhesive on these products may contaminate the sample with toluene.

Soil Description/Logging

At LUFT sites, the primary goals of boring logs are to document subsurface stratigraphy and support monitoring well design. Descriptions should be sufficient to extrapolate subsurface geology between borings and support predictions beyond the investigation area. It is also important that logging activities be within project cost constraints.

Important! Evaluation of site-assessment data is highly dependent upon subsurface geologic conditions; therefore, it is extremely important that reports of site-assessment activities contain accurate boring logs, so that future review and reconstruction of any evaluations made or conclusions drawn will be possible.

Historically, LUFT investigations have relied largely on the Unified Soil Classification System (USCS) for describing lithologic samples, using ASTM International D-2488 (see Howard 1986). The USCS/ASTM system, originally designed for geotechnical investigations, is useful for fine-grained soils with limited matrix porosity. Based on hand tests, geologists and engineers primarily describe fine-grained soils in terms of their toughness, plasticity, and dilatancy. With practice, these hand tests quickly and accurately distinguish between silts and clays, both predominant aquitard units at most LUFT sites. Therefore it is recommended that the USCS/ASTM system be used as a minimum. Additional description of coarse-grained soils is recommended in terms of texture, composition, and sedimentary structures in sufficient detail to interpret the depositional environment (e.g., Berg 1979).

All logged intervals should, at a minimum, begin with ASTM/USCS Group Symbols and Group Names, followed by Munsell Colors, text plus hue, value, and chroma codes. For fine-grained soils (≥50% finer than #200 sieve), descriptions should continue with plasticity, toughness, and dilatancy. Descriptions should also include reaction with hydrochloric acid (HCl), soil (pedogenic) structures, cementation, root bores, and accessory minerals, as appropriate.

For coarse-grained soils or sediments (<50% finer than #200 sieve) descriptions should continue with texture, composition, and sedimentary structures. Texture should generally include total size range and modes, in millimeters (mm), grain shape, using the Powers (1953) chart for sands or USCS/ASTM for gravels, and estimated sorting. Textural descriptions should be sufficient to describe vertical grading within permeable units (e.g., fining- and coarsening-upward sequences).

Composition information should include hand-lens estimated percentages of quartz, feldspars, and rock fragments. Composition should also include accessory minerals (e.g., heavy minerals and muscovite) and fossils.

All descriptions should include field moisture content and evidence of pollution (e.g., staining, odor, sheen, PID reading). Additionally, the blow count (generally per 6 inches) can be recorded to measure the density of the subsurface.

For bedrock, descriptions include rock type, color hardness, mineralogy, fracture pattern, and any inclusions observed. Further guidance on recording field observations, including an example field log, and additional discussion regarding soil boring descriptions, can be found in Appendix B.

Management of Investigation-Derived Waste

Drill cuttings and decontamination water are typical sources of investigation-derived waste (IDW) in soil investigations. The cuttings and water must be properly containerized and stored, sampled, and analyzed for COCs, and disposed of in accordance with regulatory requirements, based on the concentration of COCs in the waste and the receiving facility.

Additional information is available online at the U.S. Environmental Protection Agency (EPA) website (USEPA 2011):

http://www.epa.gov/superfund/policy/remedy/sfremedy/waste.htm

Grouting of Soil Borings

Soil borings or DPT holes must be grouted in accordance with regulatory requirements. These requirements may vary with hole depth (e.g., above or below the water table), and different agencies allow for the use of different grouting materials (e.g., high-solids bentonite slurry, Portland cement, or cement-bentonite mixtures). Grout is typically placed into the hole from the bottom to the top using a tremie or pump to ensure that the borehole is completely filled and that bridging in the hole does not occur.

Further Reading.

ASTM International (formerly known as the American Society of Testing and Materials [ASTM]). 1990. Standard Practice for Description and Identification of Soils. D2488-90.

ASTM. 2004. Standard practice for design and installation of ground water monitoring wells in aquifers. D 5092-04.

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Chapter 15: Site Assessment
Groundwater Investigation:
Grab Groundwater Samples

September 2012

Groundwater investigations at a LUFT site are conducted to determine whether the release from the UST has migrated and impacted the water-bearing zones beneath the site. "Grab" or screening groundwater samples are not collected from monitoring wells, are typically turbid, and provide a gross understanding of groundwater quality. Several methods are available to accomplish the collection of a "grab" or screening groundwater sample without bearing the expense of installing a groundwater monitoring well. For the purpose of this section, the objective of grab groundwater sampling is assumed to be characterization of the petroleum dissolved in the groundwater. Grab groundwater samples also can be used to roughly indicate the presence of product near the water table; however, they cannot distinguish between residual (immobile) and mobile product (see Fate and Transport chapter) because the act of collecting a grab groundwater sample disturbs the soil structure and can release immobile product from the soil pores. It is important that grab groundwater results that include product not be reported as or confused with what is actually dissolved in the groundwater (see "Turbidity Issues" below).

Laboratory Analysis and Methods

The analytes and analytical methods for groundwater samples at LUFT sites are discussed in the Laboratory Analysis and Methods chapter of this Manual. In addition, the Analytical chapter provides information on testing of product samples for forensic purposes.

Direct-Push Methods

Grab groundwater samples are routinely collected using direct-push rigs (for example, Geoprobe or CPT). These methods typically rely on the emplacement by DPT of a groundwater sampler with a shielded screen to a specified depth, retraction of the sampler to expose the screen, and collection of the sample by either retrieving the entire sampler or by lowering a miniature bailer or tubing into the sampler to retrieve the sample.

There have been many generations of DPT samplers since the early 1990s. The most commonly used are Geoprobe Systems® DPT equipment and the Hydropunch™ sampling tool. These grab groundwater samples are frequently used to identify the lateral and vertical extent of a groundwater plume prior to installing monitoring wells. Care needs to be exercised to ensure that the samples are representative and are not confounded by cross-contamination or other problems. A key consideration in the choice of sampler and method of emplacement is the potential for cross-contamination of the sample from impacted soils above the water table or at the capillary fringe, or from shallower water zones. Also critical is whether the sample is to be collected across the water table or beneath the water table.

Tip: It is recommended that the stratigraphy of the target zone be assessed using continuous core or CPT before the groundwater samplers are deployed.

The use of DPT groundwater samplers is discussed in Publication No. EPA 540/R-04/005, Office of Solid Waste and Emergency Response (OSWER) No. 9200.1-51 (EPA 2005) and ASTM D6001-05 (ASTM 2005).

A recent development (as of 2010) is the availability of small-diameter "pre-packed" well screens that can be emplaced with a DPT rig (EPA 2005). The pre-pack is a polyvinyl chloride (PVC) well screen surrounded by a sand filter pack held in place by a stainless-steel mesh. The sand pack allows for development of the temporary sampling point so that turbidity of the water sample is reduced.

Open Borehole Methods

Some grab groundwater samples are collected by inserting PVC screen and riser casing into an open borehole drilled by HSA or advanced by DPT soil coring. The quality of samples collected from these temporary wells has historically been relatively low because of the occurrence of high turbidity. Those temporary wells that used pre-packed well screens can now be developed to reduce the turbidity of the groundwater samples collected.

Turbidity Issues

Grab groundwater samples collected from the smear zone at LUFT sites frequently contain petroleum-affected soil particles, sheen, or product globules as turbidity. This turbidity is an artifact of the sampling process. The smear zone is the vertical interval near the water table where both separate-phase petroleum and water are present in the soil pore spaces. The act of collecting a grab groundwater sample disturbs the soil structure, which greatly increases the petroleum-impacted soil particulates and can release immobile product from the soil pores. It has been shown that turbid samples from the smear zone are not representative of dissolved-phase concentrations, because the non-dissolved petroleum contained within the samples as turbidity is included in the analysis (Zemo 2009). Turbidity can be reduced in the field by the use of pre-packed well screens and development of temporary sampling points. Filtering of groundwater samples to be analyzed for semi-volatile constituents (e.g., TPHd/DRO or PAHs) could potentially be performed at the laboratory if a glass-fiber filter is used. Glass-fiber has been proven to not sorb dissolved hydrocarbons; however, other filter materials are not acceptable because they can sorb dissolved hydrocarbons (Foote, et al. 1997). Other turbidity-reduction procedures can be performed in the laboratory if necessary to isolate the water phase of the sample prior to analysis (see Special Handling for Turbid Groundwater Samples or Samples Containing Sheen subsection in the Laboratory Analysis and Methods chapter).

Important! Every effort should be made in the field to produce samples that are as low in turbidity as possible so that the grab groundwater results more closely represent what is dissolved in the groundwater.

Equipment Decontamination

All sampling equipment must be thoroughly decontaminated between sampling locations using either steam cleaning or non-phosphate detergent wash with double tap-water rinse and a final de-ionized water rinse. Collecting and analyzing equipment field blanks is particularly important for grab groundwater sampling programs, because a permanent sampling point is not present that would easily allow for re-sampling if equipment contamination is suspected after the analytical results are available. In addition to the potential problem of “carryover” between sampling locations, there is potential for a component of the grab groundwater sampling equipment to contribute organic compounds that can be measured as TPH. Equipment field blanks are obtained by passing distilled or de-ionized water, as appropriate, through the decontaminated sampling equipment (including single-use tubing if used).

Chapter 15: Site Assessment
Groundwater Investigation: Well Construction and Development

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Groundwater wells are installed at LUFT sites after it has been determined that groundwater has been impacted and the general location of contamination has been established, based on the information gained from groundwater screening samples. The installation of wells allows for higher quality samples and permits multiple sampling rounds.

This section discusses the design and installation of two types of wells that are commonly installed at LUFT sites: groundwater monitoring wells and groundwater extraction wells.

Legal.

Prior to installing a well but after the proper permits are obtained, the responsible professional must ensure that the design and installation are in accordance with state and local regulatory requirements. The State of California requirements for monitoring wells are found in Department of Water Resources (DWR) Bulletins 74-81 and 74-90. Each county may also have its own well standards.

Monitoring Well Design and Construction

The design of a groundwater monitoring well includes the selection of the proper target zone and the proper selection of screen size and filter pack, as discussed in subsequent sections. Monitoring wells must be designed by or under the direct supervision of a licensed professional (geologist or engineer) with current California registration and experience in hydrogeologic investigations and monitoring-well design and installation. Additionally, monitoring wells must be installed by a Water Well Drilling Contractor, C-57 license holder, in good standing with the Contractor State License Board.

Selection of Target Zone

At petroleum release sites, monitoring wells have typically been screened across “the water table” irrespective of stratigraphy. This has evolved due to the historical regulatory requirements that sheen or product at the capillary fringe be observable in the monitoring well throughout the hydraulic year. This has resulted in many sites where the shallowest monitoring wells are screened primarily across fine-grained soils, and the bottom of the screen interval sometimes crosses coarse-grained soils. These conditions can result in samples with anomalous water-level measurements and chemical concentrations.

Site stratigraphy should be understood prior to selecting target zones for monitoring well screens. This is best achieved by collecting continuous-core samples via several exploratory borings prior to installing wells. Although wells screened across “the water table” may be desirable in the source area to evaluate the presence of mobile product, most of the dissolved-phase mass will migrate away from the source area through soil units with higher relative hydraulic conductivity—interconnected pore spaces that allow water to flow through—typically coarse-grained sediments such as sand or gravel. For sites with heterogeneous stratigraphy, therefore, these coarse-grained units should be selected as target zones for monitoring wells, both within and beyond the source area.

If a well is being installed to monitor a “deeper” zone (which is presumably less impacted than the “shallow” zone), it is important to seal off the shallow zone during drilling and well installation to avoid or minimize cross-contamination or drag-down. This is particularly important in an LNAPL source area.

Selection of Screen Length, Screen Slot Size and Filter Pack

Selection of screen depth and length depends on the purpose of the monitoring well and the fluctuations in the depth to groundwater at the site. Petroleum can form a “smear zone” in soil between high and low water level elevations (see Fate and Transport chapter) and mobile product (if present) will only be measureable in a monitoring well if the well is screened across the smear zone and the water table occurs within the smear zone at the time of the measurement. If monitoring product thickness is the purpose of the monitoring well, then it is important to consider fluctuations in groundwater elevations when designing the well. For sites where groundwater elevations are stable, well screens that extend 5-feet above and below the current the water table are acceptable in most cases. However, if the smear zone at the site or data at nearby properties indicates that the water level is likely to rise or fall more than 5 feet above or below the current water table over the year or over several years, the screened interval may need to be expanded.

The proper selection of screen size and filter pack for the target zone allows for adequate well efficiency and the production of low-turbidity samples. Well design is based on the lithology of the target zone and the purpose of the well. At a minimum, the filter pack material (e.g., silica sand) and well casing material (e.g., PVC) must be non-reactive and appropriate for the subsurface chemical environment. In addition, the permeability of the well-screen slot size and filter pack should be slightly less than the permeability of the surrounding formation in order to limit sediment from entering, yet close enough to the permeability of the surrounding formation so as not to impede the natural flow of groundwater through the subsurface.

The selection of well-screen slot size and filter pack can involve a “rigorous” procedure or an “intermediate” procedure, depending on project requirements.

The rigorous approach is based on sieve analysis of soils from the target zone, which can be performed in the field. Results from the sieve analysis are employed in the classic design method presented in *Groundwater and Wells* (Driscoll 1986). The filter pack retains 70% of the target formation, and the screen retains 90% of the filter pack. This procedure and its advantages for environmental monitoring wells are documented in Reynolds and Zemo (1992 [ASTM STP 1118]).

An intermediate approach to selection of screen size and filter pack for groundwater monitoring wells is based on field experience, and does not require sieve analysis. Rather, this approach relies on visual estimates of grain-size distribution in the target zone to determine the proper filter pack and screen slot size. Based on field experience, a target zone that is comprised of silt might call for a #0/30 sand filter pack (or grain-size equivalent) and a 0.010-inch slot size screen. Target zones with silty sand or fine sand might be completed using a #2/16 filter pack (or equivalent) and a 0.020-inch slot size screen. To maximize well efficiency, medium sand or coarser target zones might be completed using #3 or #2/12 filter pack (or equivalent) and 0.030-inch slot screen.

Monitoring Well Installation

The borehole into which the well will be installed can be drilled using several methods as described above, “Soil Investigation Methods.” The typical drilling methods used for the installation of monitoring wells at a LUFT site include HSA, rotary, and sonic. The key criteria for selection of drilling methods are related to the well construction: target zone depth, inside diameter of the well casing needed for passing of pumps and sampling tools, and a borehole diameter that is at least 4 inches larger than the outside diameter of the well casing.

Monitoring wells are typically constructed with threaded Schedule 40 polyvinyl chloride (PVC) blank casing of 2- or 4-inch inside diameter. In cases of deep wells (e.g., >100 feet), Schedule 80 PVC may be used because of its greater strength to withstand the increased pressure. The inside diameter of the casing must be large enough to pass probes and purge/pump/sampling equipment; the use of 2-inch inside diameter casing has become very common with the advent of narrow pumps and sampling equipment. The well screen will usually consist of threaded machine-slotted PVC or wire-wrapped screen. The slot size for the well screen will be compatible with the filter pack and the target zone (see discussion above). The bottom of the well screen will be fitted with a threaded end cap. For deep wells, stainless-steel centralizers should be installed above and below the well screen and every 50 feet above the top of screen to ensure that there is proper annular space.

After placement of the casing and screen assembly into the borehole, the annular filter pack and annular seal is installed.

Important! Borehole stability during well installation is very important, to ensure that annular fill and seals are emplaced properly with no bridging or particle-size segregation. During the placement of the annular material, depth of the material should be continuously measured to verify proper placement and depth.

The filter-pack sand will be poured or tremied into the annular space around the well screen. The filter-pack sand is usually placed above the uppermost perforation a minimum distance of 10% of the screened interval to account for potential settlement. For example, if a well has a screened interval of 20 feet, then the filter pack should extend a minimum of 2 feet above the uppermost perforation.

The well should be pre-developed before placement of the seal. Pre-development consists of surging or agitating the water column within the well casing to promote settlement of the filter pack and the removal of gaps or bridges in the filter pack. Pre-development should be performed for at least 5 minutes and continue until the filter pack stops settling. Additional sand may need to be added to the annular space upon completion of the pre-development activities.

A seal is installed above the filter pack to prevent contaminants at the surface from migrating down into the filter pack and into groundwater. A transition seal comprised of fine-sand or bentonite chips/pellets is then poured or tremied into the annular space above the filter sand. The bentonite should be hydrated and allowed to cure in accordance with manufacturer's specifications. The thickness of the transition seal is typically 2 feet long, but may be larger depending on the overlying grout column thickness.

Tip: If a drilling method other than HSA or ARCH is used, and the borehole is exposed during installation of the monitoring well and annular material, a tremie pipe should be used. A tremie is a pipe placed into the borehole used as a funnel to prevent bridging of sand or grout between the borehole and monitoring well outer casing. Bridging may cause gaps which can settle over time and compromise the quality of the sanitary seals and other annular fill. The tremie pipe is placed at the base of the layer to be filled (i.e., at the base of the borehole for the sand filter pack, or at the top of the bentonite seal for grout placement). As the material is placed at depth, the tremie pipe is slowly raised.

A neat cement grout, cement/sand grout, cement/bentonite grout, or high-solids bentonite grout is then placed from the top of the transition seal to the ground surface. The grout seal is usually pumped or tremied into the annular space. The seal thicknesses and grout/additive/water mixtures are determined based on Department of Water Resources (DWR) Well Standards Bulletin 74-81 and 74-90, site-specific conditions, and local regulatory requirements. Depending on local regulatory requirements, an inspector may observe the mixing and placement of the grout seal. The time period that the grout must set may vary between 48 and 72 hours before the well can be developed. It is recommended that curing times be based on the manufacturer's specifications and that the lead regulatory agency be contacted in advance to determine curing requirements prior to conducting well development activities. See Figure 15-2 for an example of a monitoring well construction diagram.

Important! It is important that the required volumes of fill be calculated and compared to the real-time field amounts so that any bridging is detected and eliminated as the fill is being installed.

Surface completions can be at or below grade (e.g., traffic-rated vault or Christy box) or above-grade (e.g., steel protective stovepipe). The type of surface completion for the well is based on site-specific conditions. The objective for the surface completion design is to reduce the potential for entry of surface water runoff or foreign matter into the well and to secure the well from unauthorized entry. Surface completions often have to make up grout volume at the top of the borehole due to grout shrinkage in the annular space.

Well-completion forms must be filed with the DWR after the completion of well installation. Instructions on how to fill out a well completion report are provided on the DWR website:

http://www.water.ca.gov/pubs/groundwater/how_to_fill_out_a_well_completion_report/wcr_instruction_pamphlet_2_.pdf

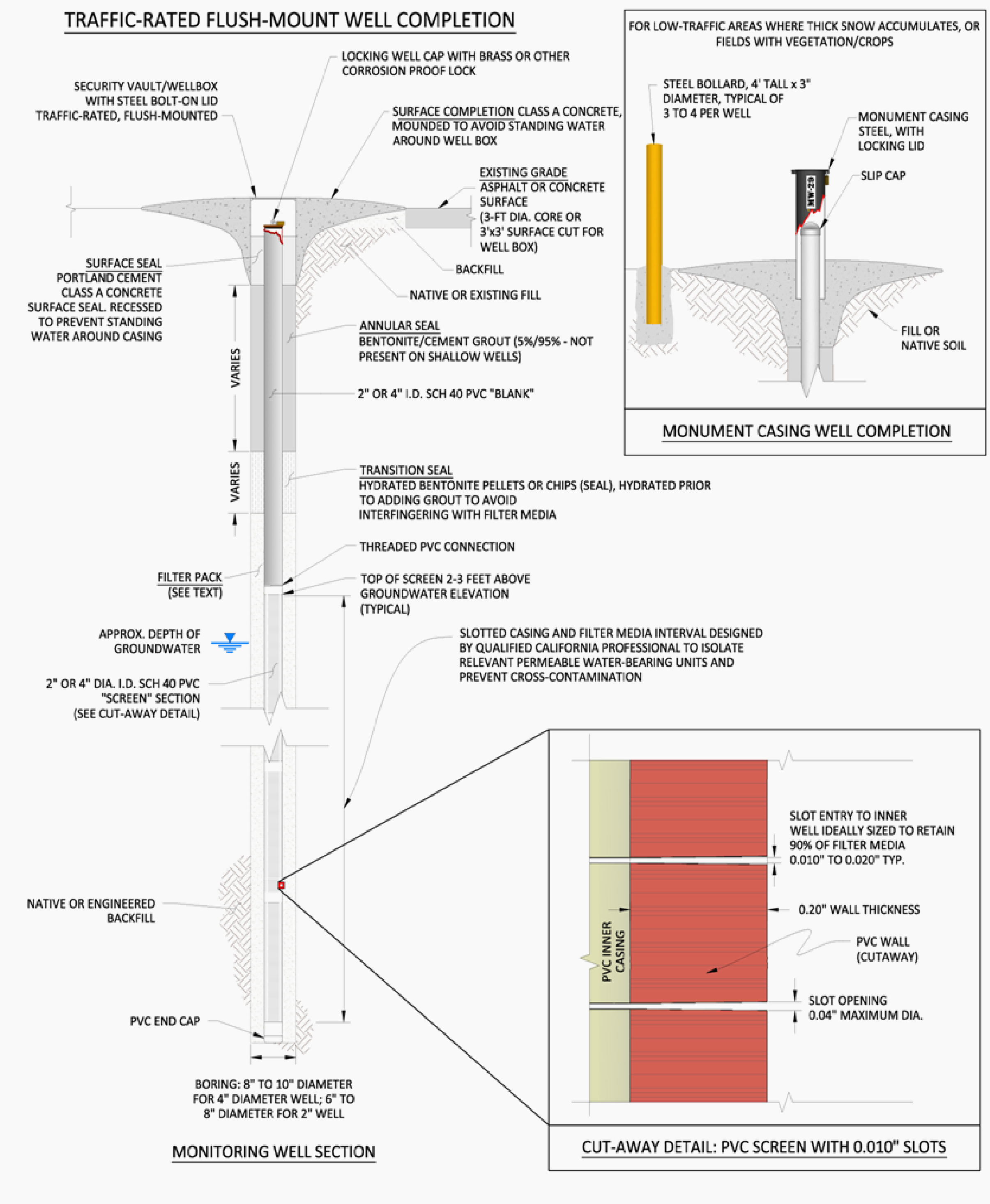
Wells installed for remediation purposes must be designed according to the planned remediation activities and site-specific conditions. This information is discussed in the Remediation chapter of this Manual. The design of such wells must be approved by the permitting agency before the wells may be installed.

Wells Designed to Monitor Multiple Zones

Often, it is desirable to monitor multiple water-bearing zones at one location to profile the vertical distribution of COCs or hydraulic head. The most common way to achieve this is to use a well cluster, where wells of different depths are installed in separate, but closely spaced, boreholes. A second way to achieve this is to install "nested" wells, where several wells of different depths are placed within one large borehole and the annular fill is emplaced in stages of filter pack and bentonite or grout seal, according to the depths of the well screens. A third way to monitor multiple zones is where one "casing" is placed in one borehole, and the "casing" has multiple sampling ports at different depths. Examples of this type are the continuous multi-channel tubing system (CMT) and the Westbay system. In these cases, the annular fill is installed in stages of filter sand and grout seal, according to the depths of the sampling ports.

The use of nested wells or multi-port systems may be controversial and should be approved by the regulatory agency. The pros of these methods are that they can be less expensive for monitoring many target zones than installing separate wells. The cons are that the correct placement of the annular fill takes great care, the grout between the filter sand intervals may shrink and leave voids in the annular space, and the destruction of nested wells is usually more difficult because multiple casings are in one borehole. Additionally, consideration should be given to multi-port systems since sampling equipment may be limited for these types of monitoring wells.

Figure 15-2: Monitoring Well Construction Diagram



REFERENCE: DRISCOLL, F.G. (1986). "GROUNDWATER AND WELLS" JOHNSON FILTRATION SYSTEMS, INC. ST. PAUL, MN. PAGE 1021.

Groundwater Extraction Well Design

There are two typical objectives for groundwater extraction wells: hydraulic containment and removal of COCs from groundwater.

The two key issues in the design of groundwater extraction wells are:

- The **inside diameter of the casing** necessary for installation of a pump of adequate size for the design flow rate, and
- Careful design of the **screened interval** (filter pack and screen slot size) for maximum well efficiency and reasonably low turbidity.

It is recommended that the rigorous approach described in Driscoll (1986) be used to design an extraction well, especially for wells that are expected to have high flow rates. Also, because water-level measurements from within the pumping well are affected by well efficiency, it is common for a small-diameter piezometer to be installed within the annulus to measure water levels in the filter pack. In soils with low hydraulic conductivity, the borehole can be over-drilled a few feet and a section of blank casing threaded to the bottom of the well screen to allow for a sump and dewatering of the target zone. The annulus against the blank casing beneath the screen should be filled with bentonite. Otherwise, the construction materials and installation methods are similar to those described for monitoring wells.

Groundwater Well Development

Selection of the appropriate well-development method depends on site-specific conditions and local regulatory requirements.

The purposes of well development are to:

- Remove sediment accumulated in the well during construction.
- Remove/mitigate borehole wall damage due to drilling.
- Allow water to flow more freely toward the well.
- Consolidate the filter pack around the well screen, remove the fines from the filter pack, and from the target zone adjacent to the filter pack.
- Provide hydraulic connection between target zone and well screen.

Note. Well development is NOT simply purging. It is an active procedure designed to accomplish the listed goals and to yield low-turbidity, high-quality samples from the well. Recent work has shown that turbid groundwater samples collected from monitoring wells in the smear zone produce unrepresentative data that are biased by the petroleum-affected turbidity (Zemo 2009).

Development of wells is usually accomplished by an iterative process that involves bailing fines from the well, surging the screen area with a surge block or other device, and over-pumping at a rate exceeding the anticipated purge rate for sampling. Various pumps can be used during well development, including submersible and air-lift. Fines should be bailed out of the well several times during development. Bailing of fines is necessary to remove them from the well and to protect pumps. This iterative process continues until the return water is observably clear. Field parameters such as temperature, specific conductance, and pH provide valuable information, but their stabilization does not indicate the completion of well development. Likewise, there is no set number of casing volumes removed that indicates the completion of well development. The bailing, surging, and pumping process continues until the produced water is visually clear.

Development of wells screened across fine-grained soils can be very time-consuming because of the low percent open area of the required slotted well screen and low transmissivity of the formation. Field staff need to spend the time required to complete the well development. If the target zone recharges too slowly, potable water can be added to the casing to assist with surging. The amount of added water must be documented so that the same volume, at a minimum, is pumped out of the well before development is completed.

Likewise, development of wells installed in mud-rotary boreholes can be time-consuming because the filter cake must be broken up and lost drilling mud recovered before development can progress.

Important! It is important to over-pump the well during development at a rate that exceeds the anticipated purge rate for well sampling or extraction.

If the well is later purged or pumped at a higher flow rate, fines can be mobilized into the well and the well will need to be re-developed.

Important! Water produced during well development typically needs to be contained, so it's important to have adequate containment onsite before the development begins (e.g., tanks or drums). Water, sediment, and other waste removed from a well during development operations must be disposed of in accordance with applicable federal, state, and local requirements.

Well Destruction

Wells can be destroyed by several methods, depending on site-specific conditions and regulatory requirements.

Legal.

DWR Bulletin 74-90 requires that monitoring well construction, alteration, and destruction reports be completed on forms provided by the California Department of Water Resources (DWR 1991). The State of California requirements for well destruction are found in DWR Bulletin 74-90.

Local agencies frequently have their own requirements for well destruction, so the responsible professional must ensure that well destruction is conducted in accordance with applicable regulatory requirements. For shallower wells, a typical method involves drilling out the casing and annular fill and pressure-grouting the resulting borehole from the bottom to the ground surface. For deeper wells or larger extraction wells, the casing can be cut from bottom to top and then the inside of the casing pressure grouted. Grouting materials must be approved by the regulatory agency, and an agency representative is typically present during a destruction event. Well destructions are documented using forms from DWR and the local agency.

Well Survey

Well locations should be surveyed for horizontal and vertical control by a California Registered Civil Engineer or licensed professional surveyor. These coordinates are typically referenced to a United States Geological Survey (USGS) datum. The *x*, *y*, and *z* coordinates for each well at a site are also required to be uploaded to GeoTracker. The coordinates should also be reported in the site assessment report. It is customary practice for the surveyor (or the well-installation geologist) to place a permanent mark on the top of casing that indicates the survey point and point where groundwater elevation measurements are routinely collected.

Chapter 15: Site Assessment
Groundwater Investigation: Monitoring Well Sampling

September 2012

Groundwater monitoring well sampling (groundwater sampling) is a critical component of LUFT site management, because trends in concentrations, natural attenuation, or the response to remediation can be monitored. Effective groundwater monitoring requires consistent methods of gauging, sampling, and sample handling and analysis. Information obtained during groundwater monitoring includes depth to groundwater, thickness of separate-phase hydrocarbons (SPH) ("free product") if present, concentrations of COCs, and measurements of general chemistry parameters.

Groundwater Sampling Frequency

Groundwater sampling frequency was previously required at LUFT sites on a quarterly basis, under state regulation. Under State Water Board Resolution 2009-0042, quarterly monitoring requirements were reduced to semi-annual or less frequent monitoring at all sites unless site-specific needs warrant otherwise (State Water Board 2009). It is the responsibility of the lead regulatory agency to make the determination and justification for more frequent monitoring based on the conditions at the site.

Laboratory Analysis and Methods

The laboratory analysis and methods for groundwater samples at LUFT sites are discussed in the Laboratory Analysis and Methods chapter of this Manual. In addition, the Analytical chapter provides guidance regarding testing for forensic purposes for product samples.

Important! To be useful, data collected during different monitoring episodes, even by different consultants or over a long period of time, must be comparable. Changes in sample collection methods or laboratories can cause deviations from previous "trends."

Gauging

Gauging a well is completed prior to sampling to determine the depth to the bottom of the casing, the depth to the water surface, and the thickness of free product (if present). Gauging is performed using electronic devices or a graduated tape treated with water- or hydrocarbon-sensitive paste. Prior to taking a measurement, adequate time should be allowed for the open well to equilibrate with atmospheric pressure. Depths are recorded to the nearest 0.01 foot relative to a surveyed reference point. If NAPL is present, the measured depth to water is to be corrected using the following formula:

$$DTW_c = DTW_m - (TSPH \times SGSPH)$$

where:

- DTW_c = Corrected Depth to Water
- DTW_m = Measured Depth to Water
- TSPH = Thickness of Separate-Phase Hydrocarbons
- SGSPH = Specific Gravity of Separate-Phase Hydrocarbons

The specific gravities of some fuels are:

- Gasoline: 0.75 gram per cubic centimeter (g/cm^3)
- Diesel: 0.81 g/cm^3
- Jet Fuel (JP-4): 0.79 g/cm^3

- Fuel Oil #2: 0.91 g/cm^3
- Fuel Oil #6: 0.96 g/cm^3

Note. If blank casing was installed below the screened interval when a well was constructed, that well is not monitored unless the water level is at least 2 feet above the base of the screened interval. Otherwise, the gauged depth to water may be incorrect, and any samples collected will include the stagnant water inside the blank casing, or water which cascaded into the blank casing after it was purged.

Potential causes of anomalous water level measurements include:

- Leaking sewer lines
- Well screened improperly
- Inaccurate survey data
- Vertical flow
- Hydraulic continuity with underground utilities

Groundwater Sampling Procedures

As with soil sampling, there are many groundwater sampling guidance documents available. "Practical Handbook of Environmental Site Characterization and Ground-Water Monitoring" (Nielsen 2006) and "Ground-Water Sampling Guidelines for Superfund and RCRA Project Managers" (EPA 2002) are two comprehensive references.

If measurable free product or sheen is present in a well, it should be recorded on the field forms and in the data summary tables. The well should not be purged and sampled under most circumstances, because the water sample concentrations would most likely not be representative of the dissolved phase. The act of purging and sampling typically mixes at least some of the product with the water, thus yielding an unrepresentative water sample. In some cases, it may be specifically desired to sample the water beneath the product, but to do so involves special sampling techniques, and often there is still a minute amount of product that gets included in the "water" sample. In these cases, special laboratory handling can be used to isolate the water phase of the sample so that the analytical results are as representative of the dissolved phase as possible (see the Laboratory Analysis and Methods chapter). In some cases, a sample of product is desired for other site assessment purposes; such a sample would be collected without purging.

To minimize the possibility of cross-contamination, purging and sampling proceed from the least contaminated to the most contaminated wells, and non-dedicated purging and sampling equipment is completely decontaminated between monitoring wells. Decontamination requires thorough washing of the equipment with an appropriate cleaning solution, rinsing it twice with clean tap water, and rinsing it a third time with deionized or distilled water.

Purging

The overall objective of groundwater sampling is to collect samples that are representative of *in-situ* groundwater conditions. Sampling of groundwater monitoring wells has traditionally involved purging as the first step to remove stagnant water in the well casing. Purging involves the removal of sufficient water from a well to ensure that the samples are representative of the groundwater in the impacted zone rather than simply standing water from within the well. Three methods are discussed below. RPs should consult with their regulator regarding acceptable methods.

Conventional Method of Purging

Three or more casing volumes of water is the traditional volume required for purging a monitoring well with a bailer or pump to remove stagnant water above the screened interval prior to collecting samples. Water-quality indicators, including pH, temperature, visual turbidity, and specific conductivity of the extracted water are monitored throughout the purging process. Purging continues until conditions are stable (i.e., the variance between sequential conductivity measurements is 10% or less). The purged volumes at which measurements are collected, the measured values, the total volume of water removed, any anomalies noted (odor, color, high sediment content, etc.), and the time purging began and ended are reported for each well. It is important that a consistent purging protocol be followed during each sampling event. Changes in sample pumps (flow), depths where purge pumps are placed, volumes removed, etc., can alter the sample results gathered during that particular sampling event.

- The casing or boring volume (i.e., water-column volume) in gallons can be calculated using the following industry standard calculations:

  Height of Water Column (in feet) = (Well Depth) – (Depth to Water)

  Water Column Volume (in gallons) = (Height of Water Column) × (Volume/foot Value of a Well Diameter)

  The following are approximate volumes of water in a casing or boring (based on well diameter) used in this water-column volume calculation:

  - 1-inch well: 0.041 gallon/foot
  - 2-inch well: 0.163 gallon/foot
  - 3-inch well: 0.367 gallon/foot
  - 4-inch well: 0.653 gallon/foot
  - Other: radius squared x 0.163 to calculate gallons per foot

  The casing volume is generally required to be recorded on a groundwater monitoring well purge form or field documentation.

- After purging, a well is generally allowed to recover to at least 80% of the static water level before samples are collected. This should be verified and noted on field documentation.
- Care should be taken not to purge slow-recharge wells dry. If that does happen, water may cascade into the well from unknown intervals, and the samples obtained may not be representative of groundwater conditions. Therefore, the rate of purging and/or the volume of water removed from wells that are historically slow to recharge are adjusted accordingly.

Low-Flow Purging

Low-flow purging (or micropurging) does not require the removal of large volumes of water. In micropurging, groundwater is pumped at a low flow rate (less than 1 liter per minute or 0.25 gallon per minute) from within the well screen. This technique minimizes the mixing of overlying stagnant casing water and water within the screened interval. In addition, sample turbidity is reduced. Water-quality indicators, including pH, temperature, dissolved oxygen (DO), oxidation / reduction potential (ORP), turbidity, and specific conductivity of the extracted water are monitored throughout the purging process within a flow-through cell (e.g., YSI® Sonde). Purging continues until conditions are stable (i.e., the variance between sequential conductivity measurements is 10% or less). The purged volumes at which measurements are collected, the measured values, the total volume of water removed, any anomalies noted (odor, color, high sediment content, etc.), and the time purging began and ended are reported for each well. It is important that a consistent purging protocol be followed during each sampling event. Changes in flow rates, depths where purge pumps are placed, volumes removed, etc., can alter the sample results gathered during that particular sampling event (Puls and Barcelona 1996; Kaminski 2003).

This low-flow technique has several advantages over traditional purging:

- Less-turbid samples are produced.
- Less volatilization occurs.
- Sampling accuracy and precision are improved.
- Low pumping rates preserve the integrity of the filter pack and well seal and reduce the movement of fine sediments into the well.
- Lower volumes of purge water requiring storage, treatment, or disposal are generated.

No-Purge Sampling

No-purge sampling is conducted by carefully lowering a bailer to the water table and allowing it to fill with minimal disturbance of the water column, without prior purging of the well (American Petroleum Institute [API] 2000).

The method is applicable at sites with unconsolidated, unconfined water-bearing units and only at wells screened across the water table. No-purge sampling should not be used at wells where free product is present. It *should* be considered for sites where high-precision sampling is not needed, e.g., for routine monitoring. It *should* be supplemented with conventional or low-flow techniques. This method is quick and inexpensive, and may eliminate the variability introduced by purging. In addition, purge-water management and disposal costs are eliminated.

Passive Samplers

A type of no-purge groundwater sampling can be performed with passive samplers. These passive samplers (passive diffusion bag samplers [PDBs] are the most commonly used) remain submerged in the monitoring well for a specified time period. The passive sampler type must be matched to the chemicals being monitored (The Interstate Technology & Regulatory Council [ITRC] 2002, ITRC 2004, ITRC 2007a).

Sample Collection

Water samples are collected using equipment which minimizes the chance of volatile constituents escaping from the sample. Submersible pumps, bladder pumps, peristaltic pumps, low-flow pumps and bailers (preferably single-use) are acceptable. Air-lift pumps may not be used. Any equipment that is not dedicated to a single well must be thoroughly decontaminated before it is used at another well.

Samples are transferred from the sampling equipment to the appropriate containers carefully, to minimize mixing with ambient air. For samples that will be analyzed for VOCs, the container is filled completely at a rate less than 100 milliliters per minute so that no headspace is present. Fill the sample container so there is a meniscus (the sample liquid rises above the lip of the sample container). Then carefully place the cap on the container and screw it down tightly. The presence of headspace can be checked for by inverting the sealed container, tapping it lightly, and looking for bubbles. If bubbles are present, that sample must be discarded and another sample collected to ensure accurate data. However, if the water or the sediment in the water contains calcium carbonate, bubbles will be generated, even in the absence of headspace. In this latter case, the usual hydrochloric acid (HCl) preservative is not added to the sample containers on subsequent samplings.

Note. Not using acid as a sample preservative affects the laboratory holding times and should be considered to avoid exceeding holding times.

Samples are collected in containers and in the quantities appropriate for the requested analysis/es. All samples are labeled, properly sealed, and preserved according to stated laboratory requirements. Proper chain-of-custody procedures need to be followed, including: no time gaps between field sampler(s), courier, laboratory, or other handler(s) of the samples. The appropriate holding times for the sample medium, analytical method, and preservative used must be strictly observed.

Note. Check with your laboratory regarding any specific sample collection, volume, preservatives, or handling procedures it might require, which may be different from standard protocols.

Decontamination

The following procedures may be used for decontaminating groundwater sampling equipment:

- **Sampling Equipment:** Sampling equipment is either a) properly decontaminated between each use, or b) dedicated to each location, or c) disposed of after each use.
    - *Reusable bailers* are steam cleaned; otherwise, one-time-use, disposable bailers are used.
    - The *cord* used with reusable bailers is discarded after each use.

    - Sampling *equipment that is not steam cleaned* is initially washed with a non-phosphate detergent, rinsed twice with tap water, and final-rinsed with deionized or distilled water. Depending on the site-specific COCs, an additional acid, base, or solvent rinse may be included.

- **Rinsate Blanks** (Equipment Blanks) are obtained by passing distilled or deionized water, as appropriate, over or through the decontaminated or single-use equipment used for sampling. They provide the best overall means of assessing contamination arising from the equipment, ambient conditions, sample containers, transit, and the laboratory (EPA 2000).

Waste Disposal

Purged groundwater and other IDW should be properly containerized, labeled, and analyzed for appropriate disposal. Information on waste disposal is available online at the EPA website (EPA 2011):

http://www.epa.gov/superfund/policy/remedy/sfremedy/waste.htm

Chapter 15: Site Assessment
Soil-Vapor Investigation

September 2012

Soil-Vapor Surveys

Soil-vapor surveys can be used for a number of purposes, including the following:

- ***Initial Site Screening***, where the objective is to assess whether VOCs are present;
- ***Site Assessment/Characterization***, where the objective is to assess the source, extent, and magnitude of impacted soil, groundwater and/or vapor;
- ***Risk Assessments***, where the objective is to assess the risk to public health, safety, and the environment;
- ***Remediation and Post-Remediation Monitoring***, where the objective is to assess remediation progress or completion; and
- ***Ongoing Monitoring*** for risk assessment, remediation monitoring, landfill gas monitoring, and background methane monitoring.

Overview of Soil-Vapor Survey Methods

There are three principal methods for collecting soil-vapor data:

- Active
- Passive
- Flux Chamber

Each method offers advantages and disadvantages, which are briefly described below. The design and protocols of a soil-vapor survey program are dependent upon the objectives of the program, the types of contaminants anticipated to be present, and the site conditions. There are a variety of sampling methods and equipment designs for collecting soil-vapor samples that can potentially yield different values. If shallow low-flow or non-flow (fine-grained soil or clay) conditions exist at the site, soil-vapor analysis may not be a useful tool, and soil samples may be more applicable.

Active: The active approach consists of the withdrawal of an aliquot of soil vapor from the subsurface, typically with a sampling probe, followed by analysis of the withdrawn vapor. Analysis is often performed onsite using a variety of analytical instruments. Alternatively, soil-vapor samples can be stored in gas-tight containers and analyzed at an off-site laboratory. The active method is quantitative and values are reported in concentration units (e.g., parts per million by volume [ppmv], micrograms per liter [μg/L] –vapor). This approach is the most common soil-vapor collection method for a number of reasons, including ease of sample collection, opportunity for real-time data to direct further sampling, and the ability to acquire quantitative measurements.

Passive: The passive approach consists of the emplacement of an adsorbent into the subsurface and subsequent removal and analysis of the adsorbent. The absorbent is typically placed in the upper end of an inverted container having an open bottom. Measured values cannot be reported as concentrations, only as total adsorbed mass (e.g., micrograms [μg]) or in some form of relative units, because the amount of vapor that comes into contact with the adsorbent is unknown. Due to this limitation, passive surveys are useful for qualitative purposes only. Because one effect of the adsorbent is to concentrate the soil vapor, this approach offers advantages over the active approach in locations of low vadose-zone permeability and at sites with lower contaminant concentrations (less than 0.1 μg/L-vapor). However, contaminants must still have an appreciable vapor pressure to be detected by this method. The technique requires two visits to the field, one to deploy the adsorbents and a second trip to retrieve them, and does not allow for the acquisition of real-time data.

Flux Chambers: Flux chambers consist of an enclosed chamber that is placed on the surface for a specific period of time. Vapor concentrations are measured in the chamber after a period of time. This method is also quantitative and yields both concentration data in the chamber and flux data (mass/area-time). Flux chambers are the least common soil-vapor survey method, and are typically used only for risk-based applications when direct vapor fluxes out of the subsurface are desired.

The protocols for soil-vapor sampling most commonly followed in California are described in DTSC's *Guidance for the Evaluation and Mitigation of Subsurface Vapor Intrusion to Indoor Air (Vapor Intrusion Guidance)* FINAL October 2011. .

Additional details on soil-vapor sampling can also be found in the ITRC vapor-intrusion guidance (ITRC 2007b) available online at: http://www.itrcweb.org/Documents/VI-1.pdf and in API 2005 available online at: http://www.api.org/ehs/groundwater/lnapl/soilgas.cfm .

Laboratory Analysis

The analytical methods selected for a soil-vapor investigation are dependent upon the regulatory requirements and data quality objectives (DQOs) for a given site. Fixed labs, mobile labs, or field monitoring equipment may be suitable for the purpose, provided that the method detection limits and quality assurance/quality control (QA/QC) are appropriate for the intended use of the analytical results.

The target analytes and analytical methods for vapor samples for petroleum sites are discussed in detail in the Laboratory Analysis and Methods chapter.

Soil–Vapor Survey Design for LUFT Sites

Site Assessment/Characterization Applications

A soil-vapor survey can be used to characterize the source of the release and provide an indication of whether there is impacted soil or groundwater at the site. When characterizing the source of the leak, it is important to realize that certain components of an UST system are more likely to fail than others. For example, the tops of USTs where bungholes or man-ways are present, seams in USTs, seams in asphalt or concrete surfaces, elbows in the piping runs, and dispensers are typical sources of leaks. In addition, the base of a tank pit and associated piping can often be source zones due to the pooling of leaked substances. The sampling program should cover the most likely sources.

Soil-Vapor Method: The active soil-vapor method is most typically employed. The passive soil-vapor method can also be used, especially in locations with limited access and at sites where relatively low concentrations of VOCs are expected.

Sample Location and Spacing: The sampling locations and grid spacing should be sufficiently small to encounter areas of former USTs, piping, dispensers, etc., and any areas of gross contamination. When historical data regarding the layout of a UST system are unavailable, a useful strategy is to collect samples in a grid pattern. For a typical service station, a grid spacing of ~50 feet is reasonable. For more detailed site assessment/characterization, a sample spacing of 10 to 20 feet is reasonable in the source area.

Collection Depth: Soil-vapor samples are typically collected from 5 to 15 feet bgs to assess surface and UST releases. The chosen depth will be dependent upon the suspected source and what is being assessed: soil and/or groundwater. To assess the vertical extent of contamination, collect samples every 5 to 10 feet, depending on the depth to groundwater at the location of highest concentration.

Vapor Intrusion Assessments

Soil-vapor surveys are used during vapor-intrusion assessment to determine whether vapors are migrating from impacted soil and/or groundwater into the breathing zone.

Per the Case Closure Policy, sites may be excluded from a vapor-intrusion pathway assessment if a sufficient thickness of clean, aerobic soils exists between the volatiles source and the receptor. For groundwater sources, soil TPH must be less than 100 mg/kg throughout the either 5- or 10-foot-thick clean zone (thickness depends on groundwater benzene concentration). If oxygen is shown to be present in soil vapor at levels of 4% or greater, the minimal separation distance is reduced to 5 feet for all groundwater sources.

Soil-Vapor Method: The active method is most commonly used. Passive soil-vapor methods are not applicable, since they are non-quantitative. Permanent probes/implants offer the advantage of assessing transient effects that could affect contaminant vapor flux rates. Surface flux chambers may also be used.

Sample Location and Spacing*:* Enough samples should be collected to allow a representative estimate of the average flux to the base of the existing or future structure. For receptor assessment with existing structures or a high certainty of the location of future structures, samples should be collected near or under the structure. If the goal is to characterize the entire site, samples should be collected in the locations of highest contaminant concentrations (if known) in addition to a site-wide grid pattern.

Collection Depth: For active soil-vapor programs, samples should initially be collected from 5 feet bgs or 5 feet below existing or future building foundations, if applicable, unless there is reason to suspect shallower contamination. If the vapor concentration at 5 feet exceeds screening levels in the Case Closure Policy, a vertical profile of the soil vapor at shallower depths may be appropriate. Samples from shallower depths are more subject to infiltration of surface air and variability due to transient effects. If soil-vapor data are collected from depths less than 5 feet bgs, additional sampling events may be appropriate to ensure representative values.

Sample Frequency: Typically, one or two sampling events following installation of the probes are sufficient to assess the risk pathway. If measured concentrations are at least 10 times below the applicable screening levels, only one sampling event should be necessary. In some situations, additional sampling events may be appropriate, e.g., for shallow sampling depths.

Use of Tracers and Measurement of the Tracer; Oxygen, and Carbon Dioxide in Soil Gas: All samples collected from a depth of 5 feet or shallower should have a tracer applied at the surface to verify that there is a good annular seal. In addition, both oxygen and carbon dioxide should be measured to provide an indication of aerobic/anaerobic conditions. Oxygen can be accurately measured in the field using a hand-held analyzer such as a Landtech GA-90/GEM-2000 or RKI-brand Eagle. The portable meter should be calibrated at a low oxygen concentration (4%) and at a higher concentration (21%) to ensure accurate readings. Alternatively, samples can be sent to an off-site laboratory for analysis.

Post-Remediation Assessment & Contaminant Monitoring

Soil-vapor surveys can also be used to determine whether a remedial action has been successful or can be used to monitor residual contamination. Sample spacing and collection depth will be dependent upon the objective of the monitoring and upon the size of the remediation area. For risk assessment and remediation monitoring, use the respective protocols described previously, but with semi-permanent probes/implants that are sampled multiple times over the course of the project.

Chapter 15: Site Assessment
Lessons Learned

September 2012

Introduction

Notice to the Public: This chapter contains many ideas for "lessons learned." Some of these items have been discussed; however, many still require input. Please submit input or comments to luftmanual@onesullivan.com.

Anomalous Water-Level Data

Spaghetti Contours – What do these tell us?

We will consider "spaghetti contours" to be a site plan showing groundwater elevations which do not make sense. These contours will include water-level elevations in nearby wells which are not consistent and from which there cannot be calculated any obvious flow direction or gradient.

There are numerous reasons why this might occur at a site, and these can be categorized into two basic categories: operator error and hydrogeologic site conditions.

Examples of Operator Error:

- Attempting to contour water-level elevations using data obtained from multiple aquifers (perched, water table, confined) or from aquifers with larger vertical upward or downward gradients.
- Collecting water-level data before wells have had time to equilibrate after opening well cap.
- Failing to measure depths to water with sufficient speed in areas with significant tidal influences.
- Using measurements from wells which have filled with sediment or from wells which have become plugged in some manner. Sediment can block off a water-bearing zone and alter the water-level measurements (this effect can be gradual or show up immediately).

Examples of Hydrogeologic Site Conditions Causing Error:

- Abrupt changes in stratigraphy across a site, such as a stream channel meandering with coarse material adjacent to and interlaced with fine-grained material.
- Pods of low-permeability material can create a semi-confined condition in an otherwise water-table (unconfined) aquifer. The results can be water-level elevations that don't track evenly across a site.
- Wells located next to buried utilities where well perforations have hydraulic continuity with the utility backfill.
- Wells located near and in continuity with a former or current UST pit (can result in anomalous high or low water levels).
- Perched water zone on a portion of a site.
- Wells perforated across two or more water-bearing zones with different hydraulic heads.
- Well measurements taken immediately after a major rainfall event and before the aquifer system has time to equilibrate.
- Some of these issues can be easily resolved by graphing the water elevations each monitoring period and comparing the new elevations with the historical water-level monitoring data. It will be very apparent which well elevations track consistently with each other and which wells do not. When a well does not track consistently, seek out a reason.

Consistent Data Points

If the depth-to-water-level measurement in a monitoring well or wells is always the same, or varies very little, when other wells at a site show variance, this could signal that water levels have fallen below the screened interval of the monitoring well and that only residual water in the well's end cap is being measured. In this case, water-level measurements should be compared with the known total depth of the well, or the very bottom depth of the well should be measured and compared to the water-level results.

Anomalous Gradients

If data from one or more adjacent or nearby sites to the site being monitored differ significantly from what the data show for the site in question, it is possible that well casings have been cut, that they sank due to high traffic in the area, or that they were not accurately surveyed for top-of-casing elevation. It is appropriate to attempt to determine if this is the case when trying to explain anomalous water levels or flow directions at a site.

Issues with Computer-Generated Groundwater Contour Maps

Many computer-generated contour maps do not allow for professional geologic interpretation of a site's specific features, which should be taken into account prior to drawing groundwater contours.

Inadvertently Sampling Sheen or Non-Dissolved Petroleum

Collecting groundwater samples within the smear zone often results in the inadvertent collection of sheen or non-dissolved product in the sample due to (even minor) turbidity caused by the very act of sampling itself. This occurs both in groundwater monitoring wells and in grab-groundwater samples. Inclusion of a non-dissolved component has been documented to cause reported concentrations of analytes in groundwater to be biased high. Every effort should be made to avoid sampling sheen and to reduce sample turbidity in the field so that analytical results are more representative of the dissolved-phase concentrations in groundwater. If a sample containing sheen or petroleum-impacted turbidity is to be analyzed, laboratory procedures can be used to minimize (but not likely eliminate) the non-dissolved component in the sample (see Special Handling for Turbid Groundwater Samples in the Laboratory Analysis and Methods chapter). The laboratory report and the consultant's table of results should note that the sample contained sheen or high turbidity, which will assist with interpretation of the data. If a sample of sheen is collected for other purposes, then it is important that the analytical results not be characterized or reported as "dissolved."

Semi-Confined Aquifers

The two ends of the spectrum of types of aquifers are *confined* and *unconfined* (with *semi-confined* in between). Semi-confined aquifers are partially confined by soil layers of low permeability, through which recharge and discharge can still occur. Unconfined aquifers are sometimes also called water-table or *phreatic* aquifers, because their upper boundary is the water table (*phreatic* surface). The shallowest aquifer at a given location is typically (but not always) unconfined, meaning it does not have a confining layer (an aquitard or aquiclude) between the aquifer and the surface. Unconfined aquifers usually receive recharge water directly from the surface from precipitation or from a body of surface water (e.g., a river, stream, or lake) with which they are hydraulically linked. The water table is located above the upper boundary of confined aquifers, which are typically located below unconfined aquifers.

If the distinction between confined and unconfined is not clear geologically (in the case where it is not known whether a clear confining layer exists, or if the geology is more complex, i.e., fractured bedrock), the value of storativity returned from an aquifer test can be used to determine whether an aquifer is confined or unconfined (although aquifer tests in unconfined aquifers should be interpreted differently from those in confined aquifers).

Confined aquifers have very low storativity values (much less than 0.01, and as little as 10^{-5}), which means that the aquifer is storing water using the mechanisms of aquifer matrix expansion and the compressibility of water, which are typically both very small quantities. Unconfined aquifers have storativities (typically called "specific yield" for unconfined aquifers) greater than 0.01 (1% of bulk volume). Unconfined aquifers release water from storage by draining the pores of the aquifer, which can release relatively large amounts of water (up to the drainable porosity of the aquifer material).

Important! When installing monitoring wells in a water-bearing zone that is either confined or semi-confined, it is important to take into account that, very often, the initially measured water level in the boring will rise up to much shallower levels. If proper monitoring-well design and construction techniques are not employed during monitoring-well installation, the data collected from the well may not be reliable.

Previous Release Now Trapped below Current Water Levels

An investigator cannot necessarily assume that the LNAPL smear zone will occur only at or near the current groundwater table. Fluctuating groundwater levels may create a zone of entrapped LNAPL well below, and disassociated from, the current water table. This can happen when released LNAPL migrates to the groundwater table during a period of lower groundwater levels followed by a period of rising groundwater levels. As groundwater levels rise, this LNAPL may become entrapped far beneath the groundwater table.

In order to initially assess the potential for the occurrence of LNAPL below the current water table, the investigator should try to understand the relationship between the timing of the petroleum releases at the site and historic groundwater levels beneath the site. If evidence suggests that petroleum has been released at the site during periods when groundwater levels were significantly lower than current levels, which could occur during periods of drought or low precipitation, then the potential occurrence of LNAPL below the current groundwater table should be considered during the site assessment.

Common indications of entrapped or submerged LNAPL during site-assessment activities are:

- The occurrence of very high concentrations of dissolved petroleum hydrocarbons in groundwater (i.e., near solubility concentrations) without free-phase product or sheen being observed on top of the groundwater.
- Concentrations of dissolved constituents that are significantly higher in “deeper” site wells as compared to “shallow” site wells.
- The absence of a smear zone at the water table during drilling but the appearance of LNAPL in monitoring wells after their installation.
- The absence of a smear zone at the current water table but the presence of LNAPL in soils well below the water table during soil sampling.

The presence of high TPH concentrations or LNAPL in soil samples well below the current water table with no evidence of LNAPL in shallower samples in a particular boring suggests that lateral migration of the LNAPL took place at a time when the water table was at the depth where the sample was collected. This can be useful in providing an indication of when the release occurred (at a time when the water table was deeper).

Important! The assessment of submerged LNAPL is important to properly evaluate the site and develop an efficient plan for site remediation. If its effective solubility is high enough, submerged LNAPL is potentially a significant source of dissolved constituents to the groundwater, and can lead to inefficient site remediation efforts if not detected and evaluated.

Changes in Groundwater Flow Direction

The evaluation of groundwater flow direction is an important component of site assessment, especially if groundwater has been impacted. Groundwater flow direction is often fairly consistent beneath a site, with minor fluctuations observed due to seasonal changes. In some cases, however, significant changes in groundwater flow direction are observed, and can be attributed to a number of variables, including:

- Tidal effects.
- Groundwater levels beneath a site located near the ocean coastlines and bays or near tidal channels are often significantly affected by the ocean tides. Tidal studies where groundwater levels in monitoring wells are continuously monitored over a period of time (often during spring or neap tides) can be conducted to evaluate tidal effects. Collecting water-level measurements over a period of time covering a full tidal cycle

can usually provide confirmation of whether the tidal effect is present at a site and what the approximate lag time is between the nearest tidal waters and the site.

- Seasonal gaining/losing streams.
- Groundwater levels can be significantly affected by seasonal recharge of groundwater from streams and channels during wet periods or by seasonal discharge of groundwater into streams and channels during dry periods. Sites near surface water bodies should be evaluated for potential gain and/or loss conditions.
- Human-caused changes in groundwater flow directions.
- Pumping of groundwater in nearby wells, including cyclic pumping or seasonal pumping, can significantly affect groundwater flow direction.
- Leaking pipes and water mains can create groundwater mounding beneath a site. The mounding can produce changes in groundwater flow direction or the occurrence of a radial groundwater flow direction.
- Inaccurate groundwater level measurements and, in some cases, damage to well casings at the surface (e.g., change in reference elevations) can produce erroneous changes in groundwater flow direction. If sudden changes of groundwater flow direction are observed, review of groundwater level measurements and well conditions on field sheets is generally recommended as an initial evaluation.

Note. Water levels at many sites track the water levels of nearby surface waters, including lakes, rivers, and streams. Most of these water bodies have historical water-elevation data that can be used to evaluate historical trends. This is a different phenomenon from that of gaining/losing streams, and is also different from normal seasonal groundwater fluctuations.

When to Redevelop a Monitoring Well

Redevelopment is generally appropriate under the following conditions:

- Sediment accumulation in well.
- Well produces less, slower recharge.
- Groundwater contours have become erratic without known cause.

Anomalous Detections of "TPH"

"TPH" as measured using modified EPA Method 8015 is not sensitive to the actual constituents present in the sample, and therefore organic compounds other than petroleum can be quantified and reported by the laboratory in the GRO, DRO, and ORO ranges. VOCs such as chlorinated solvents can be reported as "TPHg/GRO." Laboratory contamination can be reported in any of the TPH ranges. Natural organics and biodegradation by-products can be reported in the "TPHd/DRO" or "TPHmo/ORO" range. Semi-volatile organics such as coal tar or creosote can be reported as "TPHd/DRO" or "TPHmo/ORO". These detections are often flagged by the laboratory as "does not match standard," but the concentrations are reported anyway.

Important! It is important to review the chromatograms to evaluate the source of the anomalous detections, and not to assume that the reported detections are petroleum.

Importance of Good Record-Keeping and Field Notes

Another common pitfall is relying on differing interpretations by multiple geologists/loggers when creating cross-sections or making geological interpretations of a site. To avoid this pitfall, review existing logs prior to drilling new borings. Ensure that the current geologist/logger is aware of previous observations and is familiar with standard procedures, including the USCS.

It is also important to ensure that important information noted on field notes makes it into the report and respective tables. For example, when known contamination is sampled, it is important that this information be represented in the report.

Additionally, good record-keeping may include copies of chromatograms for both samples and the standards used for the analyses. Chromatograms should be requested with the data and may be crucial for site assessment over time, including analyzing the site for distribution of hydrocarbon compounds and indications of natural attenuation. Depending on its data-retention policy, the laboratory may destroy its data after a certain period of time. Therefore, chromatograms and data will be unrecoverable.

Creation of Vertical Conduits by Improper Drilling and Well Installation/Destruction Methods

Drilling, well installation, and well destruction are important common components of site-assessment activities. If performed incorrectly, these activities have the potential to create vertical conduits which can allow contaminants to migrate vertically, increasing impacts to soil and/or groundwater.

Some examples of the formation of vertical conduits are:

- **Unsealed Boreholes:** Investigative boreholes that are left open can allow LNAPL to move into the boring and then downward through the open borehole annulus. This is especially likely to occur if the borehole is located in or near source areas. After completion, boreholes should be sealed as soon as possible using proper materials and methodology.
- **Improper Annular Well Seals:** Well seals that are improperly designed or improperly installed provide inadequate protection from groundwater. Annular well seals should be designed in accordance with California Monitoring Well Standards (DWR 1991). Well-seal design should take into account various subsurface factors, including lithological changes (clay zones), location of aquifers and/or groundwater-bearing zones, and location of source areas, including impacted soil materials and LNAPL. Use of improper seal materials and improper installation techniques can lead to shrinking or cracking of the seal and bridging of materials, both of which can create open areas adjacent to well casings.
- **Improper Screen Locations/Intervals**: Improper screen locations, including installing long screened segments across impacted zones (both saturated and unsaturated), and screens that extend across different aquifers or zones of groundwater, can enhance the vertical migration of contaminants.
- **Improper Destruction of Wells:** Improperly destroyed wells can leave open vertical conduits in the subsurface. Wells should be destroyed in accordance with California Well Standards (DWR 1991).

Chapter 15: Site Assessment
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Chapter 16: Laboratory Analysis and Methods

September 2012

Scope of This Chapter

The scope of this chapter is to introduce the recommended analytes and laboratory methods for analyzing soil, groundwater, and soil vapor at petroleum hydrocarbon release sites in the State of California.

Introduction

The purpose in analyzing samples of environmental media (i.e., soil, groundwater, soil vapor) is to acquire quantitative information (concentrations) regarding the petroleum hydrocarbon constituents and related chemicals (e.g., fuel additives) at a leaking underground fuel tank (LUFT) site. These data are then used to assess the lateral and vertical extent ("distribution") of petroleum constituents, and to assess risk to human health, safety, and the environment posed by the petroleum constituents.

This chapter of the LUFT Manual provides recommendations for analysis of soil, groundwater, and vapor, including analytes and analytical methods. The analytical recommendations herein are presented as current "best practices"; therefore, some analytes and methods are different from those contained in regional or local guidance documents which may pre-date this Manual. The analytes described herein are also consistent with the Low-Threat Case Closure Policy (Case Closure Policy).

For many years, California and other states have had different approaches to analytical requirements for petroleum release sites due largely to the attempt to address the complexity of petroleum fuel mixtures. California and other states have typically focused on and required the analysis of key individual petroleum constituents because of their relatively higher toxicity and/or solubility or other properties compared to the other hundreds of hydrocarbons in the mixture. For example, for groundwater plumes, the vast majority of risk posed to human health and water quality is driven by the aromatics benzene, toluene, ethylbenzene, and xylenes (BTEX; but benzene in particular) and the oxygenate methyl tertiary butyl ether (MTBE). The BTEX compounds have relatively high toxicity and are the hydrocarbon constituents with the highest effective solubility in gasoline. MTBE (which was added to gasoline in California starting in approximately the late 1980s/early 1990s and was banned in 2004) has a very high effective solubility and relatively lower biodegradation potential; therefore, it initially created longer plumes (see Fate and Transport chapter of this Manual). MTBE has lower toxicity than benzene, but it has a low taste and odor threshold; therefore, its California Secondary Maximum Contaminant Level (MCL) is low as well. While the remaining hydrocarbons make up the majority of the mass that may be present in the product, they account for a lower risk posed to human health or groundwater quality due to their lower toxicity and/or lower mobility in the environment.

In the late 1980s, the original California LUFT Manual required the use of a "total petroleum hydrocarbons" (TPH) analysis to attempt to "screen" for these other hydrocarbons. Over the past 20 years, the scientific community has learned that the use of a "bulk" TPH analysis (such as EPA Method 8015B) provides data that are not well suited to assess risk to human health or water quality, because 1) the nature of the hydrocarbons within the "TPH" changes dramatically over time due to weathering, and 2) the TPH analysis is not specific to hydrocarbons. Therefore, the TPH analysis is best used as a site characterization tool to roughly screen for the lateral and vertical extent of the petroleum.

Based on these facts, the analytical program recommended for LUFT sites is a combination of discrete (individual) target analytes and a "TPH" analysis that is appropriate for project objectives and sample medium. The recommended program is described below and is shown on Tables 16-1 and 16-2. **Note that more analytes are recommended in this chapter than are used as "criteria" chemicals in the Case Closure Policy for the various media. The "criteria" chemicals in the Case Closure Policy are those chemicals that are the key drivers regarding potential threats to human health and water quality as determined by the State Water Board for site closure decisions. The analytes presented in this chapter are intended to ensure that site characterization is adequate.**

Note. Analytical laboratories must be certified by the Environmental Laboratory Accreditation Program (ELAP). ELAP provides evaluation and accreditation of environmental testing laboratories to ensure the quality of analytical data used for regulatory purposes to meet the requirements of the State's drinking water, wastewater, hazardous waste, and other programs.

Important! GeoTracker's uploading criteria require that laboratory data be uploaded according to the GeoTracker Electronic Deliverable Format (EDF). See the GeoTracker chapter of the Manual and the link below.

http://www.swrcb.ca.gov/ust/electronic_submittal/docs/edf_gr_v1_2i.pdf

Individual Analytes by Source Fuel Type for Soil and Groundwater

Gasoline

Based on the chemistry of gasoline (described in the Fate and Transport chapter of this Manual), the recommended individual analytes for soil and groundwater samples at gasoline release sites are as follows:

- The mono-aromatics: BTEX
- Naphthalene
- Oxygenates: MTBE and *t*-butyl alcohol (TBA)
- The lead scavengers: 1,2-dichloroethane (EDC [or 1,2-DCA]) and 1,2-dibromoethane (EDB) should also be included in the analytical suite if the gasoline release was pre-1992.

In most LUFT site settings, organic lead is not persistent unless free product (light nonaqueous-phase liquid [LNAPL]) is present; therefore, it is not necessary to routinely analyze for organic lead unless site-specific information suggests that free product could be present. If organic lead is found, it should be speciated to identify the alkyl species present. It is not necessary to analyze soil at LUFT sites for inorganic lead; decades of empirical data show that the inorganic lead concentrations which could plausibly result from the conversion of organic lead are usually not significantly above background.

The use of a gasoline-range "TPH" analysis is discussed later.

Diesel, Jet Fuel, and Other Fuel Oils

Based on the chemistry of diesel and other middle distillate fuels (discussed in the Fate and Transport chapter of this Manual), the recommended individual analytes for soil and groundwater samples at jet fuel, diesel, or other fuel oil release sites are the following constituents:

- BTEX,
- Naphthalene, and
- For heavy fuel oils such as bunker fuel (fuel oil #6), the priority pollutant polycyclic aromatic hydrocarbons (PAHs).

Regarding the PAHs, it is recommended that jet fuel and diesel releases be analyzed for naphthalene (the smallest PAH) only, because empirical data indicate that naphthalene is the only PAH likely to be present in these fuels in concentrations high enough to be a potential threat to human health or groundwater quality. The other PAHs are typically not present in jet fuel or diesel #2 at concentrations significant enough to pose a threat.

The use of a diesel- or oil-range "TPH" analysis is discussed later.

Waste (Used) Motor Oils

Fresh lubricating (motor) oils are composed primarily of C25 to C32 hydrocarbons, which are almost exclusively the branched and cyclic alkanes (aliphatics). The aromatic hydrocarbons are not present in these products before they are used in engines. Because of their very large molecule sizes and the fact that they are predominantly aliphatic, these unused oils are virtually insoluble in groundwater, are not volatile, and pose virtually no risk to human health.

However, when lubricating oils are used in engines, they pick up fuel components due to cross-leakage in the chambers and, often, trace concentrations of metals from engine wear. Waste motor oils are typically contained in a waste-oil tank, which can also contain waste cleaning products used at the service station (e.g., possibly solvents). Therefore, the recommended individual analytes for soil and groundwater in the case of a waste motor oil release are:

- BTEX,
- The 16 priority pollutant PAHs,
- Chlorinated solvents (which will include EDB and EDC), and
- Oxygenates: MTBE and TBA.
- For soil only: analysis for the five “wear metals” (cadmium, chromium, nickel, lead, and zinc) is recommended.

The use of an oil-range “TPH” analysis is discussed later.

Analytical Methods for Individual Constituents

It is recommended that the volatile analytes BTEX, naphthalene, EDC, EDB, and the oxygenates MTBE and TBA be quantified by U.S. Environmental Protection Agency (EPA) Method 8260B (or 8260C when approved) because this method uses gas chromatography-mass spectrometry (GC-MS). Other GC-photo-ionization detector/flame ionization detector (GC-PID / GC-FID) methods (e.g., EPA Method 8020) have been used in the past, but are not presently recommended because they can result in false positives or misquantifications due to peak interferences and the lack of mass-spectrometer identification. At the time of this writing, the LUFT Program has not formulated its response to the May 2010 recommendation from EPA that groundwater samples be analyzed for EDB using EPA Method 8011.

It is recommended that the 16 priority pollutant PAHs be quantified by EPA Method 8270C Single Ion Monitoring (SIM) because it is a GC-MS method and can achieve the low detection limits required for comparison to criteria in the Case Closure Policy or for site-specific human-health risk assessment. Although there are other methods that may be used for PAHs, they aren’t presently recommended because they can result in misquantifications due to peak interferences (e.g., Method 8310) or they have detection limits that are often unacceptably high (e.g., Method 8270C). If a sample is analyzed using both EPA 8260 and EPA 8270 SIM, naphthalene will be analyzed twice. Use the higher of the reported concentrations for comparing to the Case Closure Policy criteria, site-specific risk assessment, or comparison to water-quality objectives (WQOs).

It is recommended that organic lead be quantified and speciated using GC-electron capture detector (ECD) or by GC-MS. HML 939 is not recommended because it does not adequately speciate the organic lead, and can be interfered with by inorganic lead complexed onto soil organic matter.

The individual analytes and currently recommended analytical methods for soil and groundwater samples at LUFT sites are summarized in Table 16-1.

Table 16-1: Individual Analytes and Methods for Soil and Groundwater Samples at LUFT Sites

Source Fuel / Product Type	Analytes	Analytical Method(s)	Comments
Gasoline	BTEX, naphthalene, MTBE, TBA (plus EDC, EDB for pre-1992 release)[1]	EPA 8260B/C	organic lead (GC-ECD) only if pre-1992 product is present
Jet A/JP5/JP8, Diesel #1 or #2, Fuel oil #1 or #2	BTEX, naphthalene, MTBE	EPA 8260B/C	MTBE[3]
Heavy Fuel Oils (bunker fuel, etc.)	BTEX, MTBE, naphthalene	EPA 8260B/C	MTBE[3]
	16 priority pollutant PAHs[2]	EPA 8270 SIM	
Waste (Used) Motor Oil	BTEX, naphthalene, chlorinated VOCs, MTBE, TBA	EPA 8260B/C	
	16 priority pollutant PAHs[2]	EPA 8270 SIM	
	Wear Metals: cadmium, chromium, nickel, lead, zinc	EPA 6010/6020 or EPA 7000/7010	Soil only

Notes:

BTEX	Benzene, toluene, ethylbenzene, and xylene
EDB	1,2-dibromoethane
EDC	1,2-dichloroethane
Jet A	Commercial jet fuel
JP5	Jet Propellant 5, military jet fuel
JP8	Jet Propellant 8, military jet fuel
MTBE	Methyl *tertiary* butyl ether
PAH	Polycyclic aromatic hydrocarbon
TBA	t-Butyl alcohol
VOC	Volatile organic compound

1) Samples to be analyzed for lead scavengers EDC and EDB only if release is pre-1992. If age of release is unknown, analyze for both oxygenates (MTBE and TBA) and scavengers.
2) 16 priority pollutant PAHs = naphthalene, acenaphthene, acenaphthylene, anthracene, phenanthrene, fluorene, chrysene, fluoranthene, pyrene, benzo(b)fluoranthene, benzo(a) pyrene, benzo(k)fluoranthene, benzo(a)anthracene, indeno(1,2,3-c,d)pyrene, dibenz(a,h)anthracene, benzo(g,h,i)perylene.
3) MTBE to be analyzed at all LUFT sites unless regulatory agency has determined that the tank contained only diesel or jet fuel per California Health & Safety Code (H&SC) §25296.15(a).

Background Regarding Total Petroleum Hydrocarbon (TPH) Analyses

California and other states have had different approaches to analytical requirements for the bulk or "total" petroleum mixture at LUFT sites. In the 1980s, the gravimetric analysis "total oil and grease" (TOG; EPA Method 413) was replaced by "total recoverable petroleum hydrocarbons" (TRPH; EPA Method 418.1) because EPA Method 418.1 included a silica gel cleanup (SGC) and was therefore more specific to hydrocarbons. In the early 1990s, the TRPH analysis (EPA Method 418.1) was replaced for LUFT site characterization by EPA Method 8015 (purgeable and extractable "total petroleum hydrocarbons" or TPH), performed using GC-FID. EPA Method 8015 is an aggregate analysis that quantifies the total amount of organic compounds present in a sample over a selected carbon range (boiling point range). Petroleum hydrocarbons may, or may not, be present in the sample because the FID is not specific to petroleum and a sample cleanup (like SGC) is not part of the method. To address the issue of non-specificity, a SGC of the sample extract was often added prior to the extractable EPA Method 8015 analysis to isolate the hydrocarbons, but this cleanup step was inconsistently applied and inconsistently accepted by regulators. Pitfalls of the TPH analysis were widely recognized and discussed by the mid- to late- 1990s (e.g., Zemo, et al. 1995; Uhler, et al. 1998).

EPA Method 8015 provides rough information about molecule size (boiling point), but it does not provide information about which individual constituents, or hydrocarbon classes, are present in the sample. Decades of empirical data at petroleum release sites have shown that EPA Method 8015 concentrations can be poorly correlated with risk to groundwater quality or to human health. This is because weathering of the released petroleum significantly changes the constituents which are present in the "TPH," and Method 8015 does not provide adequate information to evaluate the composition of the petroleum. However, the EPA Method 8015 TPH analysis can be used for the evaluation of bulk product mobility (flow as a separate-phase liquid due to gravity), calculation of site-specific mole fraction or mass fraction of the individual constituents for fate and transport calculations, identification of source areas, and evaluating the extent of organics in soil or groundwater. If a SGC is used, the extractable TPH results can be compared to petroleum-based cleanup criteria or WQOs. The EPA Method 8015 TPH analysis can also be used to determine whether or not the soil is "clean" for evaluating the vapor intrusion pathway using the Case Closure Policy criteria.

Note that the Case Closure Policy does not contain cleanup criteria for TPH in any medium. The Case Closure Policy concludes that the potential threat to human health and water quality is adequately captured by the individual "criteria" analytes for each medium. TPH is included in the Case Closure Policy and this LUFT Manual only to ensure that site characterization is adequate.

In the rare case when a site-specific risk evaluation of "TPH" is necessary, a "fractionated" TPH analysis can be used to better characterize the actual hydrocarbon components of the TPH. A "fractionated" TPH analysis separates the sample into aromatic and aliphatic fractions and then further subdivides those fractions by carbon-size ranges. Neither the EPA nor California has its own fractionated TPH analytical method. Several states have developed analytical methods that would be technically appropriate to use on California sites (e.g., MADEP 2004a, MADEP 2004b, and WA Ecology 1997). Be aware that the carbon ranges are slightly different among the various state methods; those in the WA Ecology method are used by most states. Also, if fractionated TPH analysis is performed, it is recommended that *n*-hexane and 2-methylnaphthalene be added to the list of individual constituents for volatiles and extractables, respectively.

Therefore, there are multiple types of TPH analytical methods that can be used at LUFT sites, and selection of the appropriate method depends on how the data are to be used.

Analytical Methods for Total Petroleum Hydrocarbons

Table 16-2 provides a menu of TPH analytical methods that can be used at LUFT sites, depending on data objectives. The table shows what each method actually measures, the recommended uses for the method, and important comments about the method. As is clear from the table, the different methods yield different types of information, and therefore the appropriate method must be carefully selected to meet site-specific purposes. Details about each method are provided in following subsections.

Table 16-2: Methods for "TPH" Analyses for Soil and Groundwater Samples at LUFT Sites

EPA Method	What It Measures	Recommended Use	Comments
1664	*n*-Hexane Extractable Material (HEM; Oil & Grease), and Silica-gel Treated HEM (SGT-HEM; Non-polar Material) by extraction and gravimetry (replaced Methods 413 and 418.1 when Freon was banned)	For materials with boiling points > 85 °C. Provides gross amount of HEM or SGT-HEM. HEM provides no information about molecule class or size. SGT-HEM provides some information about molecule type (non-polar), but not aliphatic/aromatic class, and not size. **Not recommended for LUFT sites because it provides so little information and no chromatogram, and no regulatory criteria have been developed for HEM or SGT-HEM.**	**Included on this table for informational purposes only.**
8260B/C GRO (gasoline-range [or purgeable] organics by GC-MS) Recommend C5 to C12 carbon range.	All volatile organics that are purged from a sample and that are detected by a MS within in a certain boiling range (carbon range) and are quantified using a gasoline standard.	Provides gross concentration of purgeable organics within the specified carbon range. Does not provide information about molecular class. Can be used to identify source areas, for mass-fraction calculations of individual compounds, estimating bulk product mobility, or evaluating the extent of organic-impacted soil or groundwater. Can provide TICs because of MS. Chromatogram can be used to identify fuel type/ weathering.	Soil or groundwater. Can include non-petroleum purgeable organics (e.g., CVOCs). Products other than (or in addition to) gasoline may be present. Analytical results may not be comparable to EPA Method 8015B GRO.
8015B GRO (gasoline-range [or purgeable] organics by GC-FID) Recommend C5 to C12 carbon range	All volatile organics that are 1) purged from a sample and 2) detected by an FID within a certain boiling range (carbon range) and 3) quantified using a gasoline standard.	Provides gross concentration of purgeable organics within the specified carbon range. Does not provide information about molecular class. Can be used to identify source areas, for mass-fraction calculations of individual compounds, to estimate bulk product mobility, or to evaluate the extent of organic-impacted soil or groundwater. Chromatogram can be used to identify fuel type / weathering.	Soil or groundwater. Can include non-petroleum purgeable organics (e.g., CVOCs). Products other than (or in addition to) gasoline may be present.

Table 16-2: Methods for "TPH" Analyses for Soil and Groundwater Samples at LUFT Sites (Continued)

EPA Method	What It Measures	Recommended Use	Comments
8015B DRO or ORO (diesel- or oil-range [or extractable] organics by GC-FID) (**DRO**: recommend C12 to C22) (**ORO**: recommend C23 to C32)	All semi-volatile organics that are extracted from a sample and that are detected by an FID within a certain boiling range (carbon range) and are quantified using a diesel or motor oil standard.	Provides gross concentration of extractable organics within the specified carbon range. Does not provide information about molecular class. Can be used to identify source areas, for mass-fraction calculations of individual compounds, to estimate bulk product mobility, or to evaluate the extent of organic-impacted soil or groundwater. *Results should not be used to compare to petroleum hydrocarbon-based cleanup criteria or WQOs*. Chromatogram can be used to identify fuel type / weathering.	**DRO:** can be used for soil, but is not optimal for groundwater. **ORO:** used for soil only. Can include non-petroleum extractable organics (e.g., coal tars, creosote, polar by-products of petroleum biodegradation, leakage from sewer lines, natural organic matter). Products other than (or in addition to) diesel or motor oil may be present.
8015B DRO or ORO with Silica Gel Cleanup (SCG) (using a 10-gram column cleanup based on EPA Method 3630C) **(DRO with SGC:** recommend C12 to C22) **(ORO with SGC:** recommend C23 to C32)	Semi-volatile organics that are non-polar (and therefore are hydrocarbons) and that are detected by an FID within a certain boiling range (carbon range) and are quantified using a diesel or motor oil standard.	Provides the best estimate (if using 8015B) of the gross concentration of hydrocarbons present within the specified carbon range. Therefore, results *can be used to compare to petroleum-hydrocarbon-based cleanup criteria or WQOs.* Provides some information about molecular type (non-polar), but not aliphatic / aromatic class. Can be used to identify source areas, for mass-fraction calculations of individual constituents, to estimate bulk product mobility, or to evaluate the extent of petroleum hydrocarbons in soil and groundwater. Chromatogram can be used to identify fuel type / weathering.	**DRO with SGC:** can be used for soil, but is not optimal for groundwater. **ORO with SGC:** used for soil only. Cleanups can be incomplete, and should be checked using a reverse surrogate and/or chromatogram pattern. Use of 10 grams of silica gel is advised. Products other than (or in addition to) diesel or motor oil may be present.

Gasoline-Range Organics (GRO) Using Method 8015B or 8260B (Purgeables)

Soil and groundwater samples can be analyzed for gasoline-range organics (GRO) by purge-and-trap using either EPA Method 8015B (GC-FID) or modified EPA Method 8260B (GC-MS) and quantified using a gasoline standard. The organics are quantified as "gasoline," but products other than (or in addition to) gasoline may be present. This analysis can include non-petroleum organics, including chlorinated solvents. GRO results must be carefully interpreted if chlorinated solvents are known or suspected to be present. Method 8015B GC-FID has been the longer-standing of the two methods. Quantitative results from Method 8015B and Method 8260B/C may not be comparable; therefore, it is recommended that one or the other be used at a single site, and that the method not be changed during site characterization or a groundwater monitoring program. To capture the bulk of the gasoline range and also avoid overlap with the diesel range, the suggested carbon range for GRO quantification is C5 to C12. Chromatograms of samples, standards, and method blanks should be provided with the complete laboratory report. Chromatograms can be used to confirm the type of petroleum present in the sample and to assess weathering.

Diesel-Range or Oil-Range Organics (DRO or ORO) Using Method 8015 (Extractables)

Diesel-range or oil-range organics (DRO or ORO) can be analyzed using EPA Method 8015B (GC-FID). Although the organics are quantified as "diesel" and "motor oil," products other than (or in addition to) diesel or motor oil may be present, or non-petroleum organics may be present, including coal tar and creosote. This analysis does not distinguish between hydrocarbons and non-hydrocarbon organics unless a SGC is used. This extraction-based method provides some information about the carbon sizes present in the sample. The suggested carbon range for quantification of DRO is C12 to C22, quantified using a diesel fuel standard. The suggested carbon range for ORO is C23 to C32, quantified using a motor-oil standard. Chromatograms of samples, standards, and method blanks should be provided with the complete laboratory report. Chromatograms can be used to confirm the type of petroleum present in the sample and to assess weathering.

Soil samples can be analyzed for DRO, but this method is not optimal for groundwater samples. Research has shown that the hydrocarbon constituents which would comprise the dissolved phase from a petroleum release are primarily BTEX, the C9 to C11 alkylbenzenes, and the C10 to C14 PAHs (including the alkyl naphthalenes), depending on the source fuel type (see Fate and Transport chapter). These hydrocarbons would be quantified primarily within the GRO range (C5 to C12) and not the DRO range (C12 to C22). The Fate and Transport chapter also shows that hydrocarbons larger than C12 have very low effective solubility. **The ORO analysis is inappropriate for groundwater samples**, because none of the dissolved petroleum hydrocarbons would be within that carbon range (C23 to C32). If very much DRO or ORO is found in groundwater, it is an indication that a non-dissolved component (e.g., LNAPL) and/or a non-hydrocarbon component may have been included in the sample. For weathered releases, it is well established that the DRO or ORO quantification for groundwater samples reflects primarily polar non-hydrocarbons resulting from biodegradation of the petroleum, and not the dissolved petroleum hydrocarbons (Zemo, et al. 2012; Lang, et al. 2009; Zemo and Foote 2003; Lundegard and Sweeney 2004). The use of the DRO analysis for groundwater samples should be carefully considered because of the analytical imprecision and the ability to adequately evaluate the dissolved-phase petroleum hydrocarbons from most sources using GRO.

Samples analyzed by EPA 8015B for DRO or ORO can be extracted using either methylene chloride or hexane. The extraction solvent should be noted on the lab report, because the extraction solvent may impact the quantitative results, especially for weathered petroleum. Soil samples can be extracted using EPA Methods 3550, 3541, or 3546. If groundwater samples are to be analyzed, they can be extracted using EPA Methods 3510, 3520, or 3511.

As discussed below, if the DRO or ORO results are to be compared to petroleum hydrocarbon-based regulatory criteria, it is appropriate that the extracts be cleaned up with silica gel to remove or reduce the polar non-hydrocarbons that may be present in the extract so that only the petroleum hydrocarbons are analyzed.

In an effort to use fewer resources and create less waste, the State of California is seeking improvements to the DRO/ORO analysis so that a smaller sample volume and less extraction solvent are used. For example, the use of 3511/8015 would allow for collection using Volatile Organic Analysis (VOA) vials instead of 1-liter amber bottles, and would only use 5 milliliters (mL) of hexane per sample, rather than 200 mL of methylene chloride. At the time of this writing, several laboratories are investigating different extraction methods and solvents in side-by-side studies with conventional methods. These new methods may be added in the future.

Other extraction-based methods such as gravimetric EPA Method 1664 (hexane-extractable material or silica gel treated HEM) are not advised, because they provide virtually no information about the carbon ranges present.

Silica Gel Cleanup for DRO or ORO

The purpose of the DRO or ORO analysis is typically to provide quantitative data regarding the petroleum hydrocarbons present in soil or groundwater. These data are then compared to petroleum hydrocarbon-based cleanup criteria or WQOs. Research performed since the mid-1990s has shown that, without SGC, analysis by EPA Method 8015B DRO or ORO is a "total extractable organics analysis" (not a petroleum hydrocarbon-specific method) and the results can include polar non-hydrocarbons if present in the soil or groundwater. These polar compounds typically result from the intrinsic biodegradation of the petroleum; however, they can also be naturally occurring or result from sampling or laboratory artifacts (Zemo, et al. 2012; Zemo and Foote 2003; Lundegard and Sweeney 2004; Lang, et al. 2009). The DRO or ORO analysis with a SGC removes or significantly reduces the polar non-hydrocarbons and provides the data necessary to assess the hydrocarbons in the sample so that comparison to hydrocarbon-based regulatory criteria is appropriate.

The State Water Resources Control Board (State Water Board), the San Francisco Bay Regional Water Quality Control Board (S.F. Bay Regional Water Board), and the California Department of Toxic Substances Control's (DTSC's) Hazardous Materials Laboratory have previously recognized the technical issue of the inclusion of polar biodegradation metabolites when analyzing water samples for extractable TPH using EPA Method 8015B. All three bodies have issued guidance that specifically recommended the use of SGC to isolate the petroleum hydrocarbons from the biodegradation metabolites when the objective is to measure the petroleum hydrocarbons (State Water Board 2002; DTSC HML 1999; S.F. Bay Regional Water Board 1999).

It is recommended that the 3510, 3520, and 3550 extracts be cleaned up using a glass column filled with 10 grams of silica gel (in accordance with EPA Method 3630C, and using the appropriate rinse solvent) prior to the TPH analysis to minimize the polar non-hydrocarbons which may be present in the extract. For hexane extracts from the micro-extraction procedure (Method 3511), SGC can be accomplished by adding a few grams of silica gel to the vial and shaking (e.g., similar to EPA Method 418.1). However, data indicate that, for methylene chloride extracts, a column cleanup is much more effective for isolating the hydrocarbons.

The issue of polar non-hydrocarbons in groundwater is discussed in more detail in the Fate & Transport chapter.

Important! No matter what cleanup procedure is used, the laboratory control samples must demonstrate that the polar compounds have been adequately removed (e.g., by a reverse surrogate such as capric acid) and that the hydrocarbons are adequately retained (e.g., by a fresh diesel spike or a discrete hydrocarbon spike) in the cleaned-up extract.

Note that it is not possible to perform a SGC for the GRO analysis because the GRO sample is not extracted prior to the analysis, but rather is purged directly into the GC. It is possible that polar non-hydrocarbons could be contributing to the GRO concentration of a given sample; however, this is apparently not as significant a problem as with the DRO or ORO analysis because GRO concentrations are frequently non-detect at sites with biodegraded petroleum sources. Possible explanations for this difference are that 1) the polar compounds are efficiently extracted with an organic solvent such as methylene chloride, but the polar compounds may not be efficiently purged from a sample due to their very high solubility, or 2) the boiling point of many of the polar biodegradation metabolites is higher than the upper limit of the GRO range.

Special Handling for Turbid Groundwater Samples or Samples Containing Sheen

The objective of analyzing groundwater samples is typically to determine the concentrations of dissolved petroleum in the groundwater, because this is the mobile portion and WQOs are based on dissolved concentrations. It is straightforward to measure the dissolved-phase concentrations when the samples contain low turbidity (i.e., they were collected from properly developed monitoring wells). However, samples are frequently submitted to the laboratory containing turbidity or sheen, either from poorly-developed wells or from grab-groundwater screening samples collected from borings. Also, samples are sometimes collected from beneath product in a well for site-characterization purposes; these samples often include small amounts of sheen, irrespective of efforts to avoid the product in the field.

For sample locations within the smear zone, the sheen and any petroleum-affected soil particles provide a non-dissolved component included within the groundwater sample. These samples have been proven to produce unrepresentative data, because the non-dissolved component is quantified in addition to the dissolved component (e.g., Zemo 2009).

Groundwater Sampling Tip: When sampling groundwater, every effort should be made in the field to produce low-turbidity samples, including using pre-pack screens for open boring samples, redeveloping monitoring wells, low-flow purge and sampling, etc.

In cases where turbid samples or samples with sheen are collected and sent to the laboratory, attempts at reducing the impact of turbidity/sheen at the laboratory may provide higher-quality data. To focus on the dissolved constituents, turbidity may be reduced and the sheen removed or avoided by the laboratory before the sample is purged or extracted.

Samples to be analyzed for volatile (purgeable) constituents and GRO can be centrifuged or gravity-separated in the VOA vial. Samples to be analyzed for semi-volatile (extractable) constituents and DRO can be filtered (0.7-micron glass-fiber Toxicity Characteristic Leaching Procedure [TCLP] filter), centrifuged, or gravity-separated in a separatory funnel with a separation period of at least 48 hours (Zemo 2009). It has been demonstrated that the glass-fiber filter (the same as that used in the EPA TCLP analysis) does not significantly sorb dissolved petroleum hydrocarbons and therefore is recommended (Foote, et al. 1997; Lundegard and Sweeney 2004); other filter materials may sorb dissolved petroleum hydrocarbons and are not acceptable. After these procedures, the laboratory can subsample the water phase prior to purging or extraction.

Implementing these turbidity- and sheen-reduction measures will result in reported concentrations which better represent dissolved-phase petroleum in the groundwater as opposed to sheen or petroleum adhered to the soil particles. However, the sample may still include non-dissolved petroleum due to the physical limitations of these laboratory handing methods; for example, non-dissolved diesel was shown to pass the 0.7-micron TCLP filter in Zemo and Foote (2003).

Chapter 16: Laboratory Analysis and Methods
Soil Vapor

September 2012

In soil vapor, components of gasoline, jet fuel, and diesel can be analyzed using modifications of EPA Methods 8260B, TO-15, and/or TO-17, depending on the detail and detection limits needed. The advantage of these methods is that they provide for mass spectrometry (MS) identification, unlike Method TO-3, which uses GC-FID and cannot provide for compound identification. Method TO-15 requires samples to be collected in Summa canisters, and TO-17 requires samples to be collected on sorbent cartridges and analyzed after thermal desorption.

The recommended individual analytes for soil-vapor samples at LUFT sites are presented in Table 16-3 below. As with soil and groundwater, more analytes are recommended in this chapter than are used as “criteria” chemicals in the Case Closure Policy for the soil-vapor medium. The “criteria” chemicals in the Case Closure Policy (benzene, ethylbenzene, and naphthalene) are those chemicals that are the key drivers regarding potential threats to human health for the vapor-intrusion pathway as determined by the State Water Board for site closure decisions. The analytes presented in this chapter are intended to ensure that site characterization is adequate.

The Case Closure Policy allows sites to be excluded from a vapor intrusion pathway assessment if a sufficient thickness of clean, aerobic soils exists between the volatiles source and the receptor. For groundwater sources, soil TPH concentration must be less than 100 milligrams per kilogram (mg/kg) throughout the either 5- or 10-foot-thick clean zone (thickness depends on groundwater benzene concentration). If oxygen is shown to be present in soil vapor at levels of 4% or greater, the minimal clean zone is reduced to 5 feet for groundwater sources containing less than 1000 µg/L benzene. Oxygen can be accurately measured in the field using a hand-held analyzer such as a Landtech GA-90/GEM-2000 or RKI-brand Eagle. The portable meter should be calibrated at a low oxygen concentration (4%) and at a higher concentration (21%) to ensure accurate readings. Alternatively, samples can be sent to an off-site laboratory for analysis using ASTM D-1945 or D-1946.

Table 16-3: Individual Analytes for Soil Vapor Samples at LUFT Sites
(Modified EPA Methods 8260B/C, TO-15, or TO-17)

MTBE
BTEX
Naphthalene
1,2-Dichloroethane (EDC) (if pre-1992 release)
1,2-Dibromoethane (EDB) (if pre-1992 release) Oxygen (field measurement or ASTM D-1945 or D-1946)

Notes:

BTEX	Benzene, toluene, ethylbenzene, xylenes
MTBE	Methyl *tertiary* butyl ether

In addition to the petroleum-related constituents and oxygen, it is recommended that soil-vapor samples also be analyzed for the leak detector compound, and for carbon dioxide using ASTM D-1945/1946. It may be prudent also to analyze for methane using ASTM D-1945/1946 if free product is known or believed to be present.

Total Petroleum Hydrocarbons in Soil Vapor

In general, a TPH analysis is not recommended for soil-vapor samples. In cases where a site-specific evaluation of the vapor intrusion pathway is required, an analysis of TPH in soil vapor may be desired. TPH in soil vapor can be analyzed by modified EPA Method 8260B/C, TO-15, or TO-17 (C4 to C12). Because these methods are GC-MS methods, they can be used to provide additional information about the constituents present by requesting “tentatively identified compounds” (TICs) from the mass spectrometry data. Requesting TICs to be quantified is important, because the concentrations of hydrocarbons in the vapor phase of a petroleum release would most likely be dominated by the aliphatics, due to their high Henry's Law Constant (see Fate and Transport chapter). The aliphatics have much lower toxicity than the aromatic compounds. If TICs are quantified by the lab, human health risk can be evaluated for the discrete compounds detected. The MS also allows for better evaluation and subtraction of potential interfering compounds such as leak-detector compounds, non-hydrocarbons, and 1,3-butadiene.

The TPH analysis by modified EPA Method 8015B (GC-FID) provides no information about the constituents or aromatic / aliphatic classes actually present, is subject to many interferences that cannot be evaluated because of the FID, and is not recommended for soil-vapor samples.

Because there are several different calibration standards for the TPH analysis (e.g., gasoline, aliphatic mixture, etc.), the LUFT Manual advises asking the laboratory to specify on its analytical report what type of calibration standard was used for quantification.

Another alternative for site-specific risk assessment is to analyze soil-vapor samples using a "fractionated" TPH method. As with soil and groundwater samples, neither the EPA nor California has its own fractionated TPH analytical method for soil vapor samples. The MADEP air-phase petroleum hydrocarbons (APH) method (based on TO-15) (MADEP 2008) is recommended; this method uses GC-MS and provides quantitative data regarding aliphatics and aromatics by carbon ranges.

The MADEP fractions for APH are:

- Aliphatics: C5 to C8, and C9 to C12
- Aromatics: C9 to C10

These fractions are recommended for samples from LUFT sites. **If the APH method is used, *n*-hexane should be added to the individual constituent analyte list (Table 16-3) so the toxicity of the C5 to C8 aliphatic fraction will not be over-estimated.**

Important! The MADEP Air-Phase Petroleum Hydrocarbons (APH) method (based on TO-15) is the preferred method for fractionated analysis (if needed) of soil vapor for the LUFT program until Cal/EPA adopts or develops its own analytical method.

Chapter 16: Laboratory Analysis and Methods
LNAPL

September 2012

Although the following analyses are not routinely performed on LNAPL samples, important information about the nature of the LNAPL can be obtained. This information can be used to improve the understanding of site conditions and to assist with remediation design.

Physical Properties

The physical properties typically measured for LNAPL samples are: dynamic viscosity (ASTM D445), density (ASTM D1481), and surface and interfacial tension (ASTM D971). In addition to these tests on LNAPL itself, there are several types of tests that measure the relationship between the LNAPL and the soil that influence LNAPL mobility, such as: pore fluid saturation, capillary testing, and centrifugal force residual saturation (American Petroleum Institute [API] RP40, ASTM D6836, ASTM D425M).

Chemical Composition

LNAPL samples can be analyzed for chemical composition using high-resolution GC-FID (ASTM D3328), high-resolution GC-MS (ASTM D5739), or simulated distillation (ASTM D2887). In addition, review of the readily available TPH chromatograms (which should be provided by the laboratory for EPA Method 8015 TPH GRO/DRO/ORO as part of the data package) can provide information about product type and weathering. Forensic analyses are discussed in the next section.

Further Reading.

See the Fate and Transport chapter of this Manual for additional information on physical and chemical properties of LNAPL.

Chapter 16: Laboratory Analysis and Methods
Forensic Analysis

September 2012

Purpose of Forensic Analysis

Forensic chemistry is typically used at LUFT sites to identify the product type, to distinguish between two or more product plumes, or to estimate the date of release. There are many forensic tools available for petroleum investigations. The best tool(s) for application to a particular case depend(s) on the question posed, so clarity about the ultimate objective of the forensic work is important. There are many publications regarding forensic analysis for petroleum; helpful summaries include: Stout, et al. 2002; Stout, et al. 2006; Wang, et al. 2006; Wang and Christensen 2006; Bruya 2001; Kaplan 2003; Kaplan and Galperin 1996; Kaplan, et al. 1997.

Different forensic tools are better suited to different types of products or different sample media (product, soil, dissolved phase in groundwater, or in vapor). Forensic interpretations regarding petroleum releases must also incorporate impacts of environmental weathering (by evaporation, biodegradation, or solubilization) and impacts of changes in crude oil sources or refinery processes, because these factors greatly influence the composition of the mixture.

Presently, the most commonly used forensic tools for petroleum releases are

1) Chromatogram pattern matching
2) Analyses of discrete constituents or families of constituents
3) Analyses for additives or blending agents
4) Biomarkers
5) Stable isotopes

All of these tools have wide acceptance in the forensics community, and peer-reviewed literature provides many examples of their applications. This section provides a brief introduction to each of these tools and comments on their uses in various sample media. Because the vast majority of petroleum constituents have low effective solubilities in water, the dissolved phase of crude oil and most other petroleum hydrocarbon products is limited to relatively few constituents, and is similar among sources. Therefore, while many of the classic forensic tools that were developed for oil or similar products can have utility for soil samples, they are not as useful for dissolved-phase groundwater plumes.

Note. It is important to note that forensic analyses are not "standardized," but instead vary among laboratories. Most laboratories use modifications of existing ASTM or EPA SW-846 methods for their forensic analyses. Comparing data between two or more laboratories, therefore, can be challenging.

Gas Chromatogram Pattern Matching

Gas chromatogram pattern matching has been used for many decades for product-type identification. The foundation of this tool is high-resolution gas chromatography (GC), which separates constituents within a sample based primarily on boiling point (most laboratories use modifications of ASTM D3328). This forensic technique relies primarily on matching the boiling range (carbon range) and the pattern of the peaks or "humps" on the chromatogram of the unknown compound when compared to those of known standards. The boiling ranges and general chromatographic character of most refined fuels or lubricating oils is widely agreed upon by forensic experts, and there are multiple examples in the literature. The chromatographic character changes with environmental weathering of the petroleum, but in predictable ways. Chromatograms can also be used to characterize a mixture where multiple products have been released.

Discrete Constituent Analyses and Constituent Ratios

Obtaining detailed information about the discrete petroleum constituents present in a sample is a useful tool for distinguishing between products of similar boiling ranges (e.g., "Is the product a mixture of gasoline and Jet A fuel, or is it a wide-cut jet fuel such as JP-4?"). For the gasoline-range and jet-fuel range products, the workhorse tool is the "PIANO" analysis, an acronym for Paraffins, Isoparaffins, Aromatics, Naphthenes (cyclo-alkanes), and Olefins. These five families of hydrocarbon molecules have differing properties and occur in various products in differing proportions.

The PIANO analysis (ASTM D5134 or modified EPA Method 8260) quantitatively reports more than 100 hydrocarbons in the volatile range, usually up to C13 or C15. For the diesel-range and heavier products, the tools most frequently used are the "GC/MS Full Scan" (ASTM D5739), where six or more hydrocarbon families are isolated and compared qualitatively or quantitatively, and the "Extended PAH" analysis (modified EPA Method 8270 SIM), where typically up to 53 PAHs and sulfur-containing heterocyclics (e.g., dibenzothiophenes) are quantified. This includes the "parent" and alkylated PAHs of each homologous series (e.g., phenanthrene and the C1, C2, C3, and C4 phenanthrenes).

Ratios of the various PIANO components are routinely used to compare similarity among gasolines, and to potentially age-date products due to refining-process changes that significantly impact the PIANO signature. The relative proportions of the hydrocarbon families can be used to distinguish between diesels and heavier fuel oils and crude oils. The relative proportions of the extended PAHs are routinely used to distinguish petroleum sources from combustion sources (e.g., bunker fuel *vs.* creosote). Certain ratios of the alkylated PAHs can be used to compare similarity among petroleum sources. These tools are useful for product and soil samples. Their utility in dissolved-phase groundwater samples is typically a function of their effective solubility.

Further Reading.

There is recent research into the PIANO type of analysis for forensic evaluation of soil-vapor samples by modifying EPA Method TO-15 (Stout, et al. 2006).

Biomarkers

Biomarkers are "molecular fossils" where biochemicals such as sterols are transformed to biomarkers such as steranes during the geologic formation of crude oil. They reflect the crude-oil source from which the product was refined and are very resistant to weathering or refining effects. The biomarkers are typically analyzed as part of the "GC-MS Full Scan" (ASTM D5739), where the ion chromatograms are evaluated qualitatively. Some labs have developed a quantitative biomarker analysis based on a modification of EPA Method 8270 SIM. Biomarkers have been used for many years, and are routinely used to distinguish among petroleum sources, especially for crude oils and diesel-range or heavier products. Due to their low solubility (a consequence of their very complex molecular structure), biomarkers are not typically useful in a dissolved-phase groundwater plume.

Additives or Blending Agents

This forensic tool includes the alkyl lead packages (tetra ethyllead [TEL], tetra methyllead [TML], etc.) and lead scavengers (EDB, EDC) that were historically added to automotive gasolines, and oxygenates such as the ethers (MTBE, tertiary amyl methyl ether [TAME], etc.) and alcohols (TBA, ethanol) that have been blended with gasoline in recent year. These constituents are routinely used for age-dating gasoline releases. Research has shown that the alkyl leads typically degrade relatively quickly in the environment outside of the product matrix. Additives or blending agents can be present in unexpected products as a result of cross-contamination during fuel transport and storage. Lead scavengers and oxygenates are soluble, and therefore can be useful for forensic evaluation of a dissolved-phase groundwater plume.

Stable Isotopes

Stable isotopes of carbon, hydrogen, oxygen, and sulfur are relatively new forensic tools as applied in environmental investigations. These isotopes are in the signature of the crude oil and therefore reflect the crude-oil source from which the product was refined. Bulk stable isotopes have been used for decades in the petroleum industry to characterize individual crude oils. Due to recent advances in analytical techniques, it is possible to analyze product, soil, groundwater, and vapor matrices for stable isotopes on either a "bulk" or "constituent-specific" scale. The peer-reviewed literature contains many examples of forensic and remediation applications for stable isotopes, especially constituent-specific applications. Caution must be used in forensic interpretations, because certain isotopic ratios change due to biodegradation.

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Chapter 17: Risk Evaluation and Risk Management

September 2012

Scope of This Chapter

This chapter discusses the process of evaluating and managing risk at a leaking underground fuel tank (LUFT) site. It also provides criteria specified in the Low-Threat Underground Storage Tank (UST) Case Closure Policy.

Risk management is the process of making decisions about cleanup and corrective actions based on the identification, analysis, assessment, and avoidance, minimization, or elimination of unacceptable risks. A risk-based decision-making process is increasingly considered to be more appropriate and cost-effective than, yet still sufficiently protective as, decisions based either on background or non-detectable levels of constituents of concern (COCs) or on numerical criteria that have been developed without recognition of risk-assessment principles (Interstate Technology & Regulatory Council [ITRC] 2008).

Risk to human health, safety, and the environment should be considered at every phase of work at a LUFT site, from the initial discovery through the site-assessment and remediation phases. If, at any point, the conceptual site model (CSM) confirms the presence of a complete exposure pathway, evaluation of the risk associated with that pathway is necessary. The goal of the process is to ensure that management decisions for potentially impacted sites provide an adequate level of protection for human health, safety, and the environment.

Risk evaluation can be used to:

- Establish site-assessment objectives.
- Determine the need for additional site characterization.
- Determine the need for corrective action.
- Establish cleanup objectives and standards.
- Communicate with stakeholders.
- Determine the need for emergency or accelerated response.

The ITRC has developed two documents (referred to by ITRC as RISK-1 and RISK-2 [ITRC 2005, 2008]) regarding the use of risk assessment in the management of contaminated sites. These documents may be used to learn how various state agencies and regulatory bodies apply risk assessment in the process of risk management. This chapter has borrowed some concepts from these documents to describe the process of risk management. Access the documents at:

http://www.itrcweb.org/guidancedocument.asp?TID=44

For California LUFT sites, or other petroleum release sites that exhibit similar attributes, the first step in evaluating risk is to compare the site characteristics with the criteria in the State Water Resources Control Board (State Water Board) Resolution 2012-0016, Low-Threat UST Case Closure Policy (Case Closure Policy) adopted on May 1, 2012. This chapter will discuss the Case Closure Policy criteria along with some example situations when a site may not meet some of the criteria in this policy. The end of this chapter briefly discusses the traditional risk-assessment process.

Low-Threat UST Case Closure Criteria

There are four main sets of criteria in the Case Closure Policy: general criteria and three media-specific criteria (groundwater criteria, vapor intrusion to indoor air criteria, and direct contact and outdoor air exposure criteria). These four sets of criteria will be discussed in the following sections. It is important to note that this policy is flexible, i.e., if a site does not meet one of the media-specific criteria, then a site-specific evaluation may be performed for that exposure pathway to show low-threat conditions, and this policy can still be used for the other sets of criteria. Also, the sets of media-specific criteria in this policy are independent of each other, e.g., soil concentrations that are protective for the direct-contact pathway may not be protective for the vapor-intrusion pathway, and the vapor-intrusion criteria must be met separately.

General Criteria

The following outlines the general criteria that must be satisfied by all candidate sites to qualify for Low-Threat Closure.

1) **The unauthorized release is located within the service area of a public water system.** A public water system is described as one with 15 or more service connections or one which regularly serves at least 25 individuals daily at least 60 days per year.
2) **The unauthorized release consists only of petroleum.**
3) **The unauthorized ("primary") release from the UST system has been stopped.**
4) **Free product has been removed to the maximum extent practicable**, in accord with the *California Code of Regulations* (CCR), Title 23, Chapter 16, Section 2655 a-c. The objective of free product removal is to reduce or stop its migration as follows:
    - Free product shall be removed in a manner that minimizes the spread into previously uncontaminated zones by using recovery and disposal techniques appropriate to the hydrogeologic conditions at the site, and that properly treats, discharges, or disposes of recovery byproducts in compliance with applicable laws;
    - Abatement of free product migration shall be used as minimum objective for the design of any free-product removal system; and
    - Flammable products shall be stored for disposal safely and in a competent manner to prevent fires or explosions.

Definitions. **Light non-aqueous phase liquid (LNAPL**) is explained as being in three states in the subsurface: residual or immobile, mobile, or migrating. Free product is primarily equivalent to migrating LNAPL, and secondarily to mobile LNAPL. Therefore, LNAPL must be removed to the extent migration is stopped, and further removal of mobile LNAPL is required to the extent practicable at the discretion of the local agency. **Maximum extent practicable** is site-specific due to subsurface conditions, objectives for removal, and technical limitations.

5) **A CSM that assesses the nature, extent, and mobility of the release has been developed.** As discussed in the CSM chapter, developing a CSM of the contaminated media, the potential exposure pathways, and the potential receptors is an important first step in the risk-evaluation process. In addition to showing potential impacts to human health, the CSM should also include potential impacts to the environment, such as discharge to surface-water bodies. When performing initial risk screening by comparing site concentrations with concentrations in the Case Closure Policy, it is important to compare the actual site CSM with the CSM assumed by this policy.
6) **Secondary source removal has been removed to the extent practicable.** A "secondary source" is defined as petroleum-impacted soil or groundwater located at or immediately beneath the point of release from the primary source. To the **extent practicable** means implementing a cost-effective corrective action which removes or destroys in place the most readily recoverable fraction of source-area mass. It is expected that most secondary mass-removal efforts will be completed in one year or less.
7) **Soil and groundwater have been tested for methyl tert butyl ether (MTBE) and results reported in accordance with H&SC Section 25296.15.** The exemption to this requirement is where a lead regulatory agency determines that the UST that leaked has only contained diesel or jet fuel.
8) **A nuisance as defined by Water Code Section 13050 does not exist at the site.**

Definition. A **nuisance** is defined by the Water Code as anything that meets all of the following requirements:

- Is injurious to health, or is indecent or offensive to senses, or an obstruction to free use of property, so as to interfere with comfortable enjoyment of life or property
- Affects at the same time an entire community or neighborhood, or any considerable number of persons, although the extent of annoyance or damage inflicted upon individuals may be unequal
- Occurs during, or as a result of, the treatment or disposal of wastes (petroleum release in this case)

Groundwater Criteria

In accordance with State Water Board Resolution 1992-0049, the Case Closure Policy establishes criteria when groundwater concentrations exist above water quality objectives (WQOs) at the time of closure and be expected to reach the best water quality that is reasonable if background water quality cannot be restored.

The Case Closure Policy describes criteria on which to base a determination that threats to existing and anticipated future beneficial uses of groundwater have been mitigated or are *de minimis*, including cases that have not affected groundwater.

State Water Board Resolution 1992-0049, *Policies and Procedures for Investigation and Cleanup and Abatement of Discharges Under Water Code Section 13304,* is a state policy for water quality control and applies to petroleum UST cases. Resolution 1992-0049 directs that water affected by an unauthorized release attain either background water quality or the best water quality that is reasonable, if background water quality cannot be restored. Any alternative level of water quality less stringent than background must be consistent with the maximum benefit to the people of the state, not unreasonably affect current and anticipated beneficial use of affected water, and not result in water quality less than that prescribed in the water quality control plan for the basin within which the site is located. Resolution No. 1992-0049 does not require that the requisite level of water quality be met at the time of case closure; it specifies compliance with cleanup goals and objectives within a reasonable time frame.

Water quality control plans (Basin Plans) generally establish “background” water quality as a restorative endpoint. This recognizes the regulatory authority of the Basin Plans but underscores the flexibility contained in Resolution 1992-0049.

It is a fundamental tenet of this Case Closure Policy that if the closure criteria described in this policy are satisfied at an unauthorized petroleum release site, attaining background water quality is not feasible, establishing an alternate level of water quality not to exceed that prescribed in the applicable Basin Plan is appropriate, and that water quality objectives will be attained through natural attenuation within a reasonable time, prior to the expected need for use of any affected groundwater.

If groundwater with a designated beneficial use is affected by an unauthorized release, to satisfy the media-specific criteria for groundwater, the contaminant plume that exceeds water quality objectives must be stable or decreasing in areal extent, *and* meet all of the additional characteristics of one of the five classes of sites listed below. A plume that is “stable or decreasing” is a contaminant mass that has expanded to its maximum extent: the distance from the release where attenuation exceeds migration.

The following outlines the groundwater criteria specified in the Case Closure Policy.

- Only applicable to groundwater with a designated beneficial use.
- For sites with releases that have not affected groundwater, if the soil does not contain sufficient mobile constituents to cause groundwater to exceed the groundwater criteria in this policy, then the sites shall be considered low-threat sites for the groundwater medium.
- For older releases, the absence of current groundwater impact is often a good indication that residual concentrations present in the soil are not a source for groundwater pollution.

- Plumes with COCs exceeding WQOs must be stable or decreasing in areal extent, which is a contaminant mass that has expanded to its maximum extent – the distance from the release where attenuation exceeds migration.

Note: In California, many Regional Water Board basin plans have designated almost all groundwater as a potential drinking-water source, and drinking-water WQOs are applied as cleanup goals. The Regional Water Board basin plans are available at: http://www.waterplan.water.ca.gov/waterquality/basin_plan.cfm

To be considered "low threat," a plume that exceeds WQOs must be stable or decreasing in areal extent and must meet all of the characteristics of one of the five classes of sites listed below and illustrated in Figure 17-1:

Class 1. Contaminant plume that exceeds WQOs is less than 100 feet in length; there is no free product; and the nearest water supply well or surface water body is greater than 250 feet from defined plume boundary.

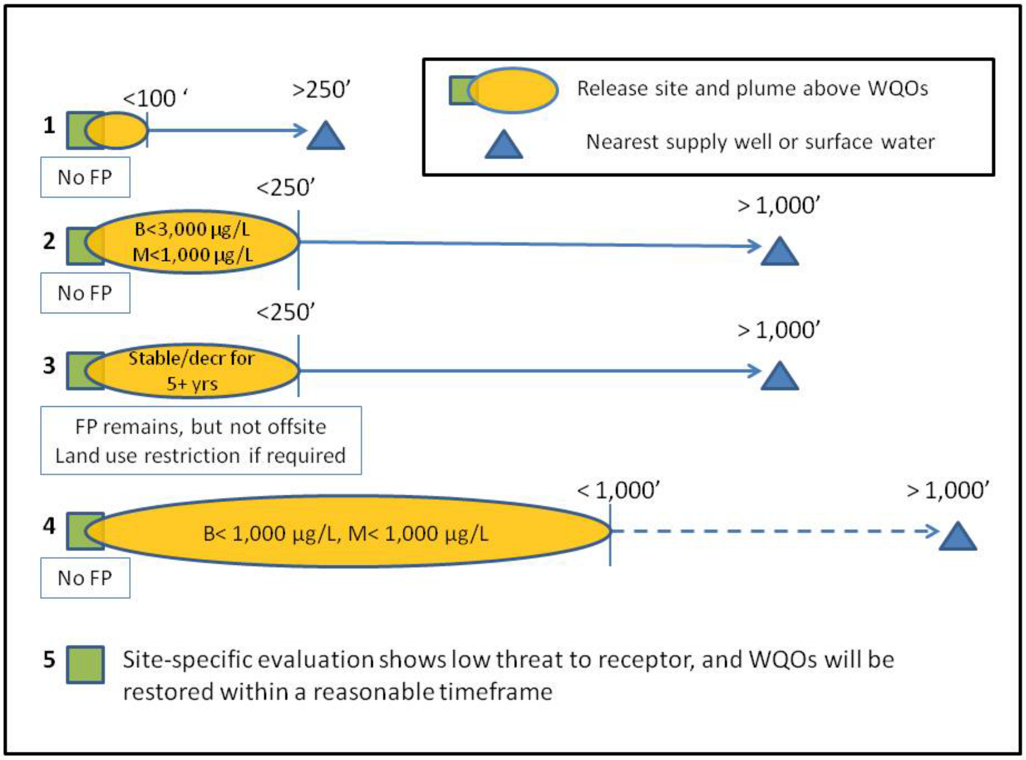
Class 2. Contaminant plume that exceeds WQOs is less than 250 feet in length; there is no free product; the nearest water supply well or surface water body is greater than 1,000 feet from defined plume boundary; dissolved concentration of benzene is less than 3,000 micrograms per liter (µg/L); and the dissolved concentration of MTBE is less than 1,000 µg/L.

Class 3. Contaminant plume that exceeds WQOs is less than 250 feet in length; free product has been removed to extent practicable; free product may still be present below the site where the release originated, but does not extend offsite; plume has been stable or decreasing for minimum of 5 years; nearest existing water supply well or surface water body is greater than 1,000 feet from the defined plume boundary; and property owner is willing to accept a land-use restriction if the regulatory agency requires a land-use restriction as a condition of closure.

Class 4. Contaminant plume that exceeds WQOs is less than 1,000 feet in length; there is no free product; the nearest water supply well or surface water body is greater than 1,000 feet from defined plume boundary; dissolved concentration of benzene is less than 1,000 µg/L; and the dissolved concentration of MTBE is less than 1,000 µg/L.

Class 5. The regulatory agency determines that, based on an analysis of site-specific conditions and under current and reasonably anticipated near-term future scenarios, the contaminant plume poses a low threat to human health and safety and to the environment, and WQOs will be achieved within a reasonable time frame.

Figure 17-1: Groundwater Plume Classes for Low-Threat UST Case Closure Policy



Notes:

B	Benzene
FP	Free Product
M	Methyl tert butyl ether
Stable/decr	Stable or decreasing in areal extent
WQO	Water Quality Objective

Figure is not to scale

Separation distances contain "safety factors" of 100% to 400% of the plume length to account for effects from preferential biodegradation of ethanol, and for any additional unanticipated plume migration (see the Fate and Transport chapter for more information on preferential degradation).

> **Note:** The taste and odor threshold of TPHd/DRO is not well documented in published literature. The most widely used value is 100 µg/L, which was originally published in 1980 by EPA as a "Suggested No Adverse Response Limit" (SNARL). The 100 µg/L taste and odor value is not derived from research performed by the EPA. The cited "1980 USEPA SNARL," which is actually for kerosene and diesel fuel #2, references only a single paper, a 1973 German paper that summarized a USSR study of USSR water-quality limits (Stofen, 1973, *Toxicology* Volume 1). It appears that the USSR study included kerosene, low-sulfur crude oil, and high-sulfur crude oil (see Table V in Stofen 1973). Therefore, the data used to create the EPA SNARL of 100 µg/L are most likely inconsistent with TPHd/DRO analytical data generated at UST sites in California.

Petroleum Vapor Intrusion to Indoor Air

Exposure to petroleum vapors migrating from soil or groundwater to indoor air may pose unacceptable human health risks. This policy describes conditions, including those in bioattenuation zones, which if met will assure that exposure to petroleum vapors in indoor air will not pose unacceptable health risks. In many petroleum release cases, potential human exposures to vapors are mitigated by bioattenuation processes as vapors migrate toward the ground surface. For the purposes of this section, the term “bioattenuation zone” means an area of soil with conditions that support biodegradation of petroleum hydrocarbon vapors.

The low-threat vapor-intrusion criteria described below apply to release sites where the release originates and has impacted or potentially impacted adjacent parcels when: (1) existing buildings are occupied or may be reasonably expected to be occupied in the future, or (2) buildings for human occupancy are reasonably expected to be constructed in the near future. This policy contains four potential exposure scenarios and describes characteristics and screening criteria associated with each scenario. (These screening criteria are presented in Appendix C.) Petroleum release sites shall satisfy the medium-specific screening criteria for petroleum vapor intrusion to indoor air and be considered low threat for the vapor-intrusion-to-indoor-air pathway if:

1) Site-specific conditions at the release site satisfy all of the characteristics and criteria of scenarios 1 through 3 as applicable, or all of the characteristics and criteria of scenario 4, as applicable (see Appendix C for a discussion of the four scenarios); or
2) A site-specific risk assessment for the vapor-intrusion pathway is conducted and demonstrates that human health is protected to the satisfaction of the regulatory agency (see the Site-Specific Risk Assessment section in this chapter and Appendix C); or
3) As a result of controlling exposure through the use of mitigation measures or through the use of institutional or engineering controls, the regulatory agency determines that petroleum vapors migrating from soil or groundwater will have no significant risk of adversely affecting human health.

Active commercial petroleum fueling facilities are not required to satisfy the medium-specific criteria for vapor intrusion to indoor air. This exception is not valid in cases where release characteristics are reasonably believed to pose an unacceptable health risk.

Direct Contact and Outdoor Air Exposure

The Case Closure Policy describes conditions where direct contact with contaminated soil or inhalation of contaminants volatilized to outdoor air poses a low threat to human health. Release sites where human exposure may occur satisfy the media-specific criteria for direct contact and outdoor air exposure and shall be considered low-threat if they meet any of the following:

- Maximum concentrations of petroleum constituents in soil are less than or equal to those listed in Table 1 of this policy (see Table 17-1 below). Both the 0-to-5-feet below ground surface (bgs) concentration limits and the 5-to-10-feet bgs concentration limits for the appropriate site classification shall be satisfied; or
- Maximum concentrations of petroleum constituents in soil are lower than the levels that a site-specific risk assessment demonstrates will have no significant risk of adversely affecting human health; or
- Mitigation measures or institutional or engineering controls are used to control exposure (to the satisfaction of the lead regulatory agency).

Important! Note that the “direct contact with contaminated soil and the inhalation of contaminants volatilized to outdoor air” criteria are not protective of other pathways. They are used only to evaluate the site for direct contact and outdoor air concerns.

Table 17-1: Concentrations of Petroleum Constituents in Soil That Will Have No Significant Risk of Adversely Affecting Human Health

Chemical	Residential		Commercial/ Industrial		Utility Worker
	0 to 5 feet bgs mg/kg	Volatilization to outdoor air (5 to 10 feet bgs) mg/kg	0 to 5 feet bgs mg/kg	Volatilization to outdoor air (5 to 10 feet bgs) mg/kg	0 to 10 feet bgs mg/kg
Benzene	1.9	2.8	8.2	12	14
Ethylbenzene	21	32	89	134	314
Naphthalene	9.7	9.7	45	45	219
PAH[1]	0.063	NA	0.68	NA	4.5

Notes:

1. Based on the seven carcinogenic poly-aromatic hydrocarbons (PAHs) as benzo(a)pyrene toxicity equivalent [BaPe]. Sampling and analysis for PAH is only necessary where soil as affected by either waste oil or Bunker C fuel.
2. The area of impacted soil where a particular exposure occurs is 25 by 25 meters (approximately 82 by 82 feet) or less.
3. NA = not applicable
4. mg/kg = milligrams per kilogram

Examples of Site Characteristics That May Not Meet All the Case Closure Policy Criteria

Some examples of sites that may not meet one or more criteria of the Case Closure Policy, and approaches for their evaluation within the context of this policy, are described below.

- **A site outside a public water supply system** (see the General Criteria sub-section for the definition of a public water supply system). These sites should be evaluated based upon the fundamental principles in this policy and a site-specific evaluation of developing water supplies in the area. The following list includes additional characteristics to consider that might result in a low-threat designation even for a site outside a public water supply.
    - Impacted groundwater that is shallower than the sanitary seal requirement for supply wells in the applicable county.
    - Impacted perched water zones are not a viable potential water supply.
    - High salinity or low yield that negate the impacted groundwater from drinking water beneficial use per State Water Board Resolution 1988-0063, or de-designated areas in various Basin Plans.
    - Groundwater plumes where WQOs will be attained through natural attenuation within a reasonable time, prior to the expected need for use of any affected groundwater.
- **Petroleum releases that are not from a UST system.** This policy may still be used to evaluate whether a petroleum-only site that is not associated with USTs is low-threat as long as the exposure assumptions are equivalent to those in this policy, or are shown to be low-threat by a site-specific analysis. For example, sites with petroleum releases from natural gas/oil field operations, pipelines, or aboveground storage tanks (ASTs) may be evaluated using this policy as long as these sites meet all of the criteria and the impacted soil is less is than 82 feet by 82 feet in areal extent (to meet the direct contact CSM), or a site-specific risk assessment shows that the impacted soil is low-risk for the direct contact pathway.
- **Sites with crude oil releases.** Although this policy was developed for fuel releases, crude oil releases could also be evaluated using this policy, as long as data for BTEX, naphthalene, and PAHs have been collected. This is because the carbon range for crude oil overlaps the combined carbon ranges for gasoline, diesel, and bunker fuel.

- **Sites containing non-petroleum chemicals (e.g., solvents) in soil**. These sites should be evaluated using a traditional risk assessment (see below).

Site-Specific Analysis for One of the Media-Specific Criteria

If a site does not meet one or more of the media-specific criteria in the Case Closure Policy, then a medium-specific analysis may need to be performed to demonstrate that the medium and its associated exposure pathways are low-threat. A few options for medium-specific risk analysis include:

- For an evaluation of direct contact and volatilization to outdoor air, calculate a more reasonable exposure concentration by averaging the measured concentrations over an appropriate (conservative) exposure area. The Case Closure Policy indicates that the maximum concentrations should be used in this analysis, so be sure to include the maximum values when calculating the average. For a residential exposure, a reasonable exposure area may correspond to the size of a small backyard.
- For the groundwater medium, use a fate-and-transport model to evaluate the potential migration and attenuation of the chemicals using site-specific calibration data when available. It is important to use models that consider mass balance whenever possible. Since petroleum hydrocarbons are highly volatile and degrade readily, many models will greatly overestimate the emission, leaching and transport rates if mass balance is not considered.
- When evaluating vapor intrusion or leaching to groundwater, use site-specific information to calculate the mass fraction of each key constituent present in the TPH for partitioning calculations (especially valuable at weathered releases or releases other than gasoline or diesel). These mass fractions can then be used in many models to calculate maximum effective solubility or maximum potential vapor concentrations in the presence of a mixture (such as TPH).
- For the vapor intrusion to indoor air pathway, use a model that considers degradation such as BioVapor (available for free from www.API.org) to model the attenuation of petroleum constituents in the vapor phase.
- For the groundwater pathway, consider the time until the facility will be closed and account for natural source depletion during that timeframe.
- For all pathways, consider future uses of the site other than residential or commercial/industrial (e.g., parks, open space).

Traditional Risk Assessment

A traditional risk assessment may need to be performed for sites that have non-petroleum chemicals present in addition to petroleum hydrocarbons. There may be other situations where a traditional risk assessment (as opposed to the tools provided in the Case Closure Policy) could be used to evaluate risk at a site.

Risk can be evaluated in several different ways, but is often evaluated using a tiered approach in which the complexity of the evaluation increases with each tier (or step) in the process. The objective of this section of the LUFT Manual is to present a tiered approach to risk assessment (i.e., start simple and increase complexity, as necessary); however, it does not prescribe specific processes for the various “tiers.”

Initial Risk Screening in Traditional Risk Assessment

Usually, the first step in the tiered risk assessment process is one in which COC concentrations in site media (soils, groundwater, vapor etc.) are compared to conservative, regulatory-derived screening levels designed to be protective under a wide range of potential exposure conditions to “screen out” those chemicals that do not need to be quantitatively evaluated site-specifically. These screening levels are developed using standard exposure assumptions and chemical toxicity criteria established by state and federal agencies. They are typically meant to be used at many different types of sites, ranging from small, relatively simple sites, such as LUFT sites, to large, highly complex sites, such as landfills or manufacturing facilities.

The regulatory screening levels are, by design, very conservative in the assumptions used to develop them. For example, usually very large source areas are assumed, and therefore the commonly used initial risk screening levels are likely overly conservative for LUFT sites. Also, most of these screening levels are calculated assuming that each petroleum constituent occurs on its own and is not part of a mixture (thereby not correctly accounting for effective solubility or effective vapor pressure), and they do not incorporate biodegradation (which has been proven to be a significant factor at petroleum release sites). Nevertheless, they are a good place to start in the risk-evaluation process.

Agencies that have developed these screening values emphasize that the intended purpose of the values is for **site screening and not for use as final cleanup levels** that must be attained at individual sites.

Initial Options for Screening Out Chemicals for Traditional Risk Assessment

At first glance, it appears that there are a number of options for initial screening levels to be used for risk assessment at LUFT sites. The first option is the chemical-specific criterion for each medium in the Case Closure Policy. For chemicals that do not have a criterion for the respective media in this policy, other screening tools may be used, including the Regional Water Quality Control Board – San Francisco Bay's (Regional Water Board – S.F. Bay) Environmental Screening Levels (ESLs), Office of Environmental Health Hazard Assessment (OEHHA) California Human Health Screening Levels (CHHSLs), EPA Regional Screening Levels (RSLs), California primary and secondary Maximum Contaminant Levels (MCLs) in groundwater and federal MCLs in groundwater. The Regional Water Board – S.F. Bay's ESLs are probably the most widely used screening levels for California LUFT sites, since they cover a wide range of exposure scenarios and use California toxicity values. The CHHSLs are also appropriate for some sites and some chemicals; however, they lack screening levels for volatile chemicals (such as most petroleum hydrocarbons) for "direct contact exposure scenarios."

California has its own set of MCLs for groundwater; therefore, the Federal MCLs should not be used for those chemicals which have MCLs established in California. Promulgated California primary and secondary MCLs are appropriate to use as screening levels for drinking water. Non-promulgated concentrations and chemicals, such as those based on Public Health Goals or narrative taste and odor properties, are not recommended as screening levels. The EPA RSLs may not be applicable to sites in California because not all of the screening numbers were developed using California toxicity values. Note that the RSLs can be adjusted to be consistent with California toxicity values if desired.

Regional Water Board – S.F. Bay Environmental Screening Levels

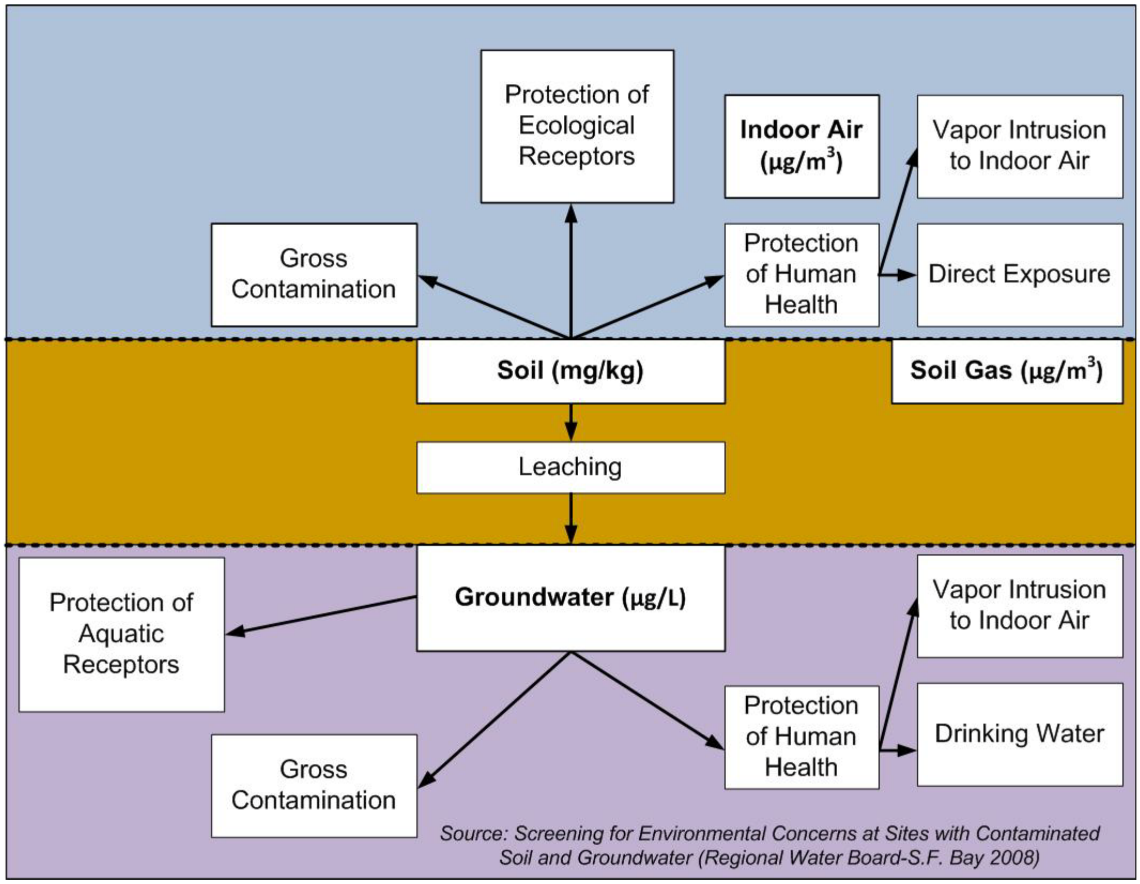
ESLs have been developed by the Regional Water Board – S.F. Bay and presented in *Screening for Environmental Concerns at Sites with Contaminated Soil and Groundwater* (Interim Final – May 2008). This report presents lookup tables for over 100 chemicals commonly found at sites with contaminated soil, groundwater, and/or soil vapor. For any particular chemical, the lookup tables present multiple screening levels designed to be protective of human health, ecological receptors, drinking-water supplies, and general nuisance conditions. Care must be given to select the appropriate tables to screen LUFT sites, and to understand the assumptions made for the COCs that have been identified. For example, the direct-contact values for the individual COCs in soil may be appropriate, but the values for soil to protect groundwater or surface water do not incorporate effective solubility or biodegradation, and therefore are expected to be overly conservative for LUFT sites. These conservative screening levels can be used to eliminate constituents of concern from further evaluation; however, if a constituent concentration exceeds the screening level, it should not be interpreted as indicating an unacceptable risk.

It is important to note that, for non-carcinogens, the ESLs assume a target hazard index (HI) of 0.2 instead of 1.0 because they assume that five COCs are present at their screening levels. This may be a very conservative assumption for LUFT sites, given the low number of COCs generally found at these sites.

Figure 17-2 shows the CSM of the environmental hazards included in the Regional Water Board – S.F. Bay's ESLs (Regional Water Board – S.F. Bay 2008). ESLs are available online at:

http://www.waterboards.ca.gov/sanfranciscobay/esl.shtml.

Figure 17-2. Conceptual Site Model for the Regional Water Board – S.F. Bay Environmental Screening Levels



Source: Screening for Environmental Concerns at Sites with Contaminated Soil and Groundwater (Regional Water Board-S.F. Bay 2008)

Maximum Contaminant Levels (MCLs)

MCLs are legally enforceable standards developed by the EPA and the State of California. MCLs correspond to the highest level of a contaminant that is allowed in drinking water. These values are typically used to screen groundwater that is a potential drinking-water source at LUFT sites, but they are not applicable to non-drinking-water sources. California MCLs can be found online at:

http://www.cdph.ca.gov/certlic/drinkingwater/pages/chemicalcontaminants.aspx
and EPA federal MCLs are online at: http://www.epa.gov/safewater/contaminants/index.html.

EPA Regional Screening Levels (RSLs)

EPA RSLs are chemical-specific concentrations for contaminants in air, drinking water, and soil that are considered to be protective for human health under assumed reasonable maximum residential or commercial/industrial exposure conditions. RSLs were initially developed for use in the EPA's Superfund/Resource Conservation and Recovery Act (RCRA) programs and have replaced the Region IX Preliminary Remediation Goals (PRGs). Some of the RSLs incorporate California toxicity parameters (especially for inhalation pathways for some chemicals); however, not all RSLs use California toxicity assumptions. RSLs are available online at:

http://www.epa.gov/region09/superfund/prg/index.html.

It is not anticipated that the RSLs will be used for LUFT sites, since the exposure pathways covered are already included in the ESLs and not all of the RSLs use the appropriate California toxicity values.

California Human Health Screening Levels (CHHSLs)

The California Environmental Protection Agency (Cal/EPA) OEHHA developed CHHSLs as required by Senate Bill 32, the California Land Environmental Restoration and Reuse Act (passed in 2000). The CHHSL screening numbers are not intended for use by regulatory agencies with the authority to require remediation of contaminated soils (OEHHA 2005). Furthermore, they do not contain soil screening levels for volatile chemicals in soil for the direct contact pathway (such as BTEX, MTBE, *t*-butyl alcohol [TBA], and naphthalene). For these reasons, CHHSLs may have limited application for LUFT sites. For the chemicals of concern at UST sites, the only screening values that are potentially useful in the CHHSLs are the soil gas to indoor air screening levels. Note that the ESLs also contain this pathway for screening purposes. CHHSLs are available online at:

http://www.oehha.ca.gov/risk/Sb32soils05.html

Options for Selecting Site Concentrations to be Compared to Screening Levels

Comparing concentrations of site-specific COCs to screening levels is performed for initial risk-screening purposes. If adequate site assessment has been completed, then maximum site concentrations below these levels indicate that the chemical is unlikely to pose a threat to human health, safety, and the environment, and that the chemical can be screened out for risk-assessment purposes.

If maximum measured concentrations exceed the screening level and the source area has been well characterized, it may be appropriate to use some type of averaging over the exposure or source area for comparing to screening levels. Making decisions based on a maximum measured concentration without considering a more realistic exposure-point concentration can result in an overestimate of risk and expensive and/or unnecessary corrective action.

One option is to use an average source concentration for comparison to the screening levels rather than the maximum detected concentration. In this case, the average may be calculated using a 95 percent upper confidence level (UCL) of the mean (if there are adequate data). If the source area is very small, areal averaging may be appropriate to estimate a more realistic exposure point concentration. For example, if the source is 2 meters (m) × 2 m in surface soil, the risk assessor may choose to average the concentration across a likely exposure area, such as the area of a small back yard for residential land uses.

After determining the constituents of concern using screening levels, a site-specific risk assessment may be conducted. Some of the things to consider in the risk assessment have been outlined above in the section entitled: Site-Specific Analysis for One of the Media-Specific Criteria.

Further Reading.

Additional guidance on risk assessments can be found on the U.S. EPA website, Waste and Cleanup Risk Assessment.
http://www.epa.gov/oswer/riskassessment/index.htm

This includes the Risk Assessment Guidance for Superfund (RAGS), Parts A through F.
http://www.epa.gov/oswer/riskassessment/ragsa/index.htm

Risk Management Decisions

Once the risk characterization is completed for an individual site, the focus turns to risk management. For example, for groundwater that is currently used (or will be used in the future) as drinking water, the risk manager considers the risk-assessment results (including exposure assumptions and uncertainties) along with other technical, legal, economic, and social considerations to reach a regulatory decision as to the appropriate actions to be taken at the site. Factors that may be important in evaluating potential actions include efficiency, timeliness, equity, administrative simplicity, consistency, public acceptability, technological feasibility, data quality, degree of certainty in future land use and groundwater use, and nature of the legislative mandate.

Risk management decisions for LUFT sites will be made on a case-by-case basis, consistent with Cal/EPA and EPA policy and guidance. The decision should take into account both site-specific and chemical-specific data. Multiple lines of evidence should be used to decrease the uncertainty in evaluating individual sites, as appropriate. Table 17-2 summarizes the basic decision logic and recommended management decisions to be considered in evaluating risk assessment results at a LUFT site. The target risks selected and the suggested actions are consistent with Cal/EPA and EPA (National Contingency Plan) recommendations for other types of sites.

Table 17-2: LUFT Risk Management Response Options

Estimated Risk/Hazard	Response	Action(s)
Risk[1] $\leq 1\text{x}10^{-6}$ and Hazard Index ≤ 1	None	No Further Action
$1\text{x}10^{-6} <$ Risk $\leq 1\text{x}10^{-4}$ or Hazard Index[2] > 1	Risk Management Decision	-Possible Monitoring -Possible Mitigation -Possible Source Remedation -Possible Site Closure
Risk > $1\text{x}10^{-4}$ or Hazard Index >1	Mitigation Source Remediation Land Use Covenants Capping Site	-Appropriate risk mitigation -Source Remediation -Isolation of constituents of concern from public and environment

Source: Department of Toxic Substances Control (DTSC) California Environmental Protection Agency (CalEPA) 2011.

Notes:

1 Carcinogenic risks are estimated as the incremental probability of an individual developing cancer over a lifetime as a result of exposure to the potential carcinogen (i.e., incremental or excess individual lifetime cancer risk).

2 A hazard index is the sum of hazard quotients for substances that affect the same target organ or organ system. Because different pollutants may cause similar adverse health effects, it is often appropriate to combine hazard quotients associated with different substances. Exposures below a health index of 1.0 will likely not result in adverse non-cancer health effects over a lifetime of exposure. However, a health index greater than 1.0 does not necessarily suggest a likelihood of adverse effects.

In addition to the specific guidance for evaluating risk assessment results, applicable statutory limits may also need to be considered in evaluating particular actions to be applied at any particular site. For example, for groundwater that is currently used as drinking water, California MCLs may need to be considered as appropriate cleanup levels. For groundwater that is not a potential source of drinking water during the timeframe in which it is anticipated that concentrations of COCs could exceed applicable water-quality criteria, again as documented in the site CSM, alternate risk management targets should be considered. In the case of recharge/discharge to surface water(s), risk management targets designed to protect aquatic life will need to be evaluated.

Risk Management and Corrective Action

When risk evaluation results indicate that potentially significant health risks may be associated with a LUFT site, corrective action may be necessary to mitigate short- and/or long-term exposure. The Remediation chapter discusses some of the various corrective actions that may be effective at reducing the risk associated with a LUFT site.

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Chapter 18: Remediation

September 2012

Scope of This Chapter

This chapter presents various approaches to remediation applicable to Leaking Underground Fuel Tank (LUFT) sites. It provides an overview of several common remedial actions that may be employed at LUFT sites, but is not intended to include all available approaches or every detail required for implementation. A review of lessons learned is included at the end of this chapter.

Remedial action may be required if the conceptual site model (CSM) for a LUFT site indicates a risk to human health, safety, and/or the environment or if the criteria adopted in the Low-Threat UST Case Closure Policy (Case Closure Policy) effective August 17, 2012, are not met (State Water Board Res. 2012-0016).

When selecting a remedial approach, it is important to evaluate and propose an appropriate remedial action that is economically viable, technically feasible, and specific to site conditions. An appropriate remedial action is any action that helps reduce or manage risk to the maximum extent practicable, while taking steps to limit activities which may have a negative impact on global climate change. The selection of remedial action(s) should be made after developing an adequate CSM, assessing risks, comparing site characteristics with the criteria in the Case Closure Policy, developing closure goals / remediation objectives, and evaluating feasible options of remediation.

Remediation involves the breaking of the source-pathway-receptor linkage via:

1) **Source Cleanup**: Reduction or elimination of risks by reducing the mass of the source and/or by changing its chemical composition to reduce its mobility or toxicity. Some commonly used technologies are excavation, soil-vapor extraction (SVE), air sparging, biosparging, dual-phase extraction, chemical oxidation, solidification / stabilization, etc.
2) **Receptor Protection**: Reduction or elimination of risks by managing the exposure to the receptor. Examples include relocation of the receptor or providing an alternate water source where the current water source is contaminated. For sites that do not currently have a receptor, but which could pose a risk if a receptor were introduced, well-implemented institutional controls (e.g., restrictions on land use) can be employed to manage future potential risks.
3) **Pathway Containment/Elimination**: These are barriers (engineering controls) preventing migration of constituents of concern (COCs) from the source or to a receptor. This is different from source cleanup, because the barriers have little effect on the rate of source depletion; they are control measures that will need to remain in place with appropriate institutional controls (ICs) until the source concentrations naturally decrease to acceptable levels or the receptor conditions change. Examples of pathway containment include: hydraulic capture by pump and treat, installation of low-permeability or permeable reactive barrier walls, sub-slab depressurization systems, etc. Engineering controls for vapor intrusion are discussed in Appendix C to the LUFT Manual.

Remedial actions are employed in either the unsaturated or saturated zones. Depending on where the CSM indicates the contamination to be present and the phase of contamination, the following remedial actions may be utilized and are discussed in further detail in this chapter. This discussion is not intended to include all of the remedial technologies available, but is a summary of several common approaches at LUFT sites.

Unsaturated Zone Remediation:

- Soil Excavation
- Soil-Vapor Extraction
- Bioventing

Saturated Zone Remediation:

- Air and Bio-Sparging
- In-Situ Chemical Oxidation
- In-Situ Groundwater Ozone Sparging
- In-Situ Groundwater Bioremediation
- Other Groundwater Remediation Technologies: Pump-and-Treat and Dual-Phase Extraction
- Natural Attenuation

As defined in the *California Code of Regulations* (CCR) Title 23 (Waters), Division 3, Chapter 16, Underground Tank Regulations Article 11 §2725, the responsible party (RP) shall propose a Corrective Action Plan (CAP) based on the information obtained during the site investigation and with concurrence from regulatory agencies. Details regarding the development of a CAP are discussed in the CAP chapter of this Manual.

Table 18-1 below presents a summary of LUFT remedial actions and the appropriate conditions for their use; subsequent sections of this chapter provide an overview of the remedial actions.

Table 18-1: Possible Remedial Actions at LUFT Sites

Contaminated Zone	Remedial Technology	When to Use	Cost
Unsaturated (Vadose) Zone	Soil Excavation	• Rapid, definitive remediation • Limited contaminated area • Shallow and soil-only contamination • Heavy clay soils (<3–5% sand or silt) which are unresponsive to other remediation technologies	Low to High, depending on site conditions
	Soil-Vapor Extraction (SVE)	• Contaminants are volatile • Contamination above groundwater table, with groundwater table > 3 feet below ground surface (bgs) • Soils have high permeability, moderate moisture content, and low organic content • May be used near a building to prevent vapor migration into the building	Moderate
	Bioventing	• Soils have high permeability and moderate moisture content • Groundwater present at depth > 3 feet bgs • Contaminants are aerobically biodegradable • Sites contaminated with mid-weight petroleum products • Site is away from basements, sewers, or other subsurface confined spaces	Moderate
Saturated Zone	Air Sparging	• Contaminants are volatile • Soils have moderate to high permeability • Contaminants are dissolved in groundwater and no free product is present • Site is away from basements, sewers, or other subsurface confined spaces • Contaminated groundwater is located in a confined aquifer • Site is away from adjacent LUFT and permitted UST facilities • Engineering controls in place to monitor potential off-site migration	Moderate

Table 18-1: Possible Remedial Actions at LUFT Sites (Continued)

Contaminated Zone	**Remedial Technology**	**When to Use**	**Cost**
Saturated Zone (Continued)	Biosparging	• Soils have high permeability • Contaminants are aerobically biodegradable • Contaminants are soluble and present mostly in groundwater • Site is away from basements, sewers, or other subsurface confined spaces	Moderate
	In-Situ Chemical Oxidation	• Rapid destruction/degradation of contaminants • Physical and chemical properties of soil and groundwater support use of technology • Often used to clean up contamination that other methods can't reach, like contamination deep within the groundwater • Used to reduce anticipated cleanup times required for natural attenuation and other remedial options • Special precautions required for use of Fenton's Reagent/hydrogen peroxide	High
	In-Situ Groundwater Ozone Sparging	• Soils have moderate to high permeability • Physical and chemical properties of soil and groundwater support use of technology • Contaminants can be oxidized by ozone • Good application for contamination in shallow groundwater • Measures taken to avoid ozone reacting with nearby tanks or other underground utilities/lines • Potential for toxic by-product generation, such as hexavalent Cr(VI), must be evaluated	Moderate
	In-Situ Groundwater Bioremediation	• Soils have moderate to high permeability • Physical and chemical properties of soil and groundwater support use of technology • Contaminants are biodegradable • Contaminants are soluble and present mostly in groundwater	Moderate
	Pump-and-Treat	• Remediation is not time-critical • Contaminants are soluble and present mostly in groundwater • Adsorption of contaminants to soil is low • Can be used to create hydraulic barrier	High
	Dual-Phase Extraction*	• Sites with clayey/silty soil where groundwater flow rates are low • Contaminants present in soils below the water table.	High
	Natural Attenuation*	• Remediation is not time-critical • Site must be evaluated for natural attenuation potential; approval from agencies is required • Subsurface conditions will not be disturbed during attenuation period • Often used after other remedial actions have taken place	Moderate

* Applicable when contamination is present in both the saturated and unsaturated zones.

Chapter 18: Remediation
LNAPL

September 2012

Federal UST Regulations (40 *Code of Federal Regulations* [CFR] 280.64), State Regulations (CCR, Title 23, Division 3, Chapter 16, Section 2655(a), and the Case Closure Policy state that "free product" (light-nonaqueous-phase liquid, or LNAPL) shall be removed "to the maximum extent practicable." The Case Closure Policy repeats sections b – d of 40 CFR 280.64 and CCR Chapter 16 Section 2655:

- Free product shall be removed in a manner that minimizes the spread of the unauthorized release into previously uncontaminated zones by using recovery and disposal techniques appropriate to the hydrogeologic conditions at the site, and that properly treats, discharges, or disposes of recovery by-products in compliance with applicable laws;
- Abatement of free product migration shall be used as a minimum objective for the design of any free product removal system [Section 2655(c) says "predominant objective"]; and
- Flammable products shall be stored for disposal in a safe and competent manner to prevent fires or explosions.

In general, removal to the "maximum extent practicable" means implementing a cost-effective corrective action which removes or destroys in place the most readily recoverable fraction of source-area mass. Stopping LNAPL migration is a clear and relatively easy-to-measure metric. Many agencies have used LNAPL thickness in a groundwater monitoring well as a metric for remediation. This is inaccurate, because the thickness of LNAPL in a monitoring well usually does not correlate with the amount of LNAPL in the formation or its mobility, due to the complex interaction of LNAPL, air, and water in soil pore spaces, as discussed in the Fate and Transport chapter. For example:

- LNAPL does not float on the water table in a uniform, high-saturation, "pancake"-like layer.
- LNAPL within the soil pore spaces is distributed above, at, and below the water table at saturations that vary vertically and laterally.
- Seasonal water-table fluctuations can cause the LNAPL to redistribute vertically, creating a "smear zone" of entrained LNAPL in the soil column between the high- and low-water levels.
- LNAPL is "mobile" when LNAPL saturation is greater than the "residual saturation."
- Not all mobile LNAPL necessarily migrates, but LNAPL must be mobile in order to migrate (ITRC 2009). Migration will not occur unless a driving head is present.
- The thickness of LNAPL that collects in a well is not equivalent to the thickness of LNAPL in the soil adjacent to the well due to complex differences in capillary pressures. A well may act as a collection point for LNAPL due to the pressure differential between the formation and ambient air.
- Once a smear zone has formed, the apparent thickness of LNAPL in a well will increase at times of lower water levels and will decrease at times of higher water levels.

Based on an understanding of the complexities of LNAPL conditions in the subsurface, it is important to set realistic LNAPL remedial objective(s) and metrics (discussed in further detail in the LNAPL Remedial Performance Metrics section below) and select the appropriate LNAPL remedial technology(ies) to achieve the objectives, all of which must be consistent with the CSM. It is also important to realize that, even under ideal conditions, only a portion of the total volume of the LNAPL release will be recoverable and that some portion of the LNAPL mass will remain in the subsurface in the immobile or residual phase.

LNAPL Remediation Approaches

There are three general objectives for remediating LNAPL: (1) to abate migration of LNAPL from the impacted area to unimpacted areas, (2) to remove mass, and (3) to mitigate the source of soluble or volatile constituents that partition from the LNAPL at concentrations that pose a threat to human health or the environment. These objectives are achieved by recovering mass, controlling mass, or by implementing a LNAPL phase change (ITRC 2009). It may be necessary to implement a combination of the LNAPL remedial actions to achieve remedial objectives. The following subsections are excerpted from the December 2009 ITRC document entitled *Evaluating LNAPL Remedial Technologies for Achieving Project Goals* and summarize LNAPL remediation approaches and performance metrics.

LNAPL Mass-Recovery Technology

LNAPL mass-recovery technologies directly recover LNAPL via physical removal and are the most frequently used technologies for LNAPL remediation. Examples of mass-recovery technologies include excavation or hydraulic recovery (e.g., LNAPL pumping or skimming, or dual-phase extraction) or technologies such as absorbent materials which are changed out periodically, etc. Hydraulic recovery may be pursued with or without flow augmentation by using remedial techniques that reduce LNAPL viscosity or interfacial tension (e.g., surfactants or solvents), thereby enhancing LNAPL flow.

LNAPL mass-recovery technologies address saturation-reduction-based LNAPL remedial objectives, which can be a key objective for a migrating plume. With the exception of excavation, which can achieve LNAPL removal (subject to logistical and practical limits), LNAPL mass recovery using pumping or skimming technologies is limited to reducing LNAPL saturation to residual saturation. At residual saturation, LNAPL will not flow and, therefore, hydraulic recovery is no longer possible. At residual saturation, the LNAPL will not migrate.

LNAPL Phase-Change Technology

LNAPL phase-change technologies do not directly remove LNAPL from the environment, as is the case for LNAPL mass-recovery technologies. Instead, LNAPL phase-change technologies exploit the tendencies of the individual constituents within the LNAPL to partition to either the vapor phase or the dissolved phase by increasing the rates of volatilization or dissolution of the LNAPL constituents by engineered means. Those LNAPL constituents are biodegraded or captured in the vapor or dissolved phase and removed from the subsurface. As the individual constituents are removed from the LNAPL, its composition is changed by loss of those constituents, and eventually the remaining LNAPL will become significantly less volatile and/or less soluble .

LNAPL phase-change technologies are primarily applicable to composition-sensitive LNAPL remedial objectives, which are usually a key objective where groundwater and vapor concentrations are to be reduced. For example, SVE is a phase-change technology because it drives the volatile constituents (approximately <C15) out of the LNAPL and into the vapor phase, where they are recovered. Certain of these low molecular weight constituents are typically targeted due to their threat to human health or water quality (e.g., small aromatics such as benzene). With LNAPL phase change comes some mass removal and therefore some saturation reduction. These technologies may therefore have some secondary application for saturation-based LNAPL remedial objectives.

LNAPL phase-change technologies are not limited by residual LNAPL saturation, because they do not depend on the presence of mobile LNAPL. Some LNAPL phase-change technologies are more elaborate to design and implement than LNAPL mass-recovery technologies, and their costs and limits may be not be as well understood as those of LNAPL mass-recovery technologies. Thus, LNAPL phase-change technologies may be more costly to design and deploy, but strategic / targeted application may minimize such limitations and possibly shorten the overall LNAPL remediation life cycle.

LNAPL Mass-Control Technology

LNAPL mass-control technologies stabilize migrating LNAPL by reducing the LNAPL saturation via blending a binding agent within the LNAPL zone (mixing technologies) or by physically blocking LNAPL migration (containment technologies). Such technologies alone may satisfactorily meet the remedial objective or can be used in combination with LNAPL mass-recovery and/or LNAPL phase-change technologies. Additional long-term operation and maintenance and stewardship requirements may also be warranted, depending on site conditions and property use. Specifically, LNAPL mass-control technologies are primarily suited for saturation-based LNAPL remedial objectives by limiting mobility or eliminating migration. The containment technologies are limited in applicability to LNAPL saturations in excess of residual saturation, since at residual saturations the LNAPL body is, by definition, immobile. In some instances, mixing technologies may also reduce cross-media impacts (e.g., recharge infiltration and leaching through the LNAPL zone) since some binding agents (e.g., Portland cement) can reduce the soil permeability of the LNAPL zone.

LNAPL Remedial Performance Metrics

For each LNAPL remediation goal, one or more "performance metrics" are defined. Performance metrics are measurable characteristics that relate to the remedial progress of a technology in abating the concern. The different LNAPL remediation technologies function differently and, therefore, the performance metrics used to demonstrate progress toward and achievement of the LNAPL remediation goal depend on the technology used. Ideally, each performance metric has a predetermined value that describes when the technology has reached the limits of beneficial application. That is the end-point metric for the technology chosen. Table 18-2 lists example performance metrics for hypothetical LNAPL remediation goals.

Table 18-2: Example LNAPL Remediation Performance Metrics

Example Performance Metrics	Description/Comments
LNAPL transmissivity	Hydraulic recovery is likely ineffective for plumes exhibiting low LNAPL transmissivity.
LNAPL/water recovery ratio	Ratio of unit volume of LNAPL recovered per unit volume of water. Decreasing ratio indicates decreasing recovery effectiveness.
LNAPL/vapor recovery ratio	Ratio of unit volume of LNAPL recovered per unit volume of vapor. Decreasing ratio indicates decreasing recovery effectiveness.
Limited/infrequent in-well LNAPL thickness	Stated LNAPL thickness goal or LNAPL thickness typically not observed in monitoring well under average site conditions. Indicative that LNAPL is not consistently recoverable and the majority of remaining impacts are residual.
Decline-curve analysis	Analysis of unit volume of LNAPL recovery or recovery rate per unit time. Declining curve indicates decreasing recovery effectiveness.
Unit cost per gallon LNAPL recovered	Increasing cost/gallon of LNAPL recovered indicates decreasing cost-effectiveness.
Soil concentration/soil concentration profile	Soil concentrations in LNAPL area meet regulatory criteria, or desired soil concentration profile demonstrated.
LNAPL saturation profile	Comparison of saturations before and after treatment to demonstrate reduced saturations.
LNAPL body footprint stabilized	Comparison of LNAPL plume footprint at a selected water-level elevation before and after treatment to demonstrate non-increasing footprint size.
Dissolved-phase plume stabilized	If exhibited, then it is an indication of a stable LNAPL body.
No first LNAPL occurrence in down-gradient well	LNAPL never entering a monitoring well installed outside of LNAPL body is evidence of stable LNAPL conditions.
Dissolved-phase concentration	Concentrations reduced to regulatory standard at a compliance point.
LNAPL composition	Reduced mole fraction of volatile or soluble LNAPL constituents.
Vapor-phase concentration	Concentrations reduced to regulatory standard at a compliance point.

Source: ITRC – *Evaluating LNAPL Remedial Technologies for Achieving Project Goals*, December 2009.

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Remediation in the Unsaturated Zone: Soil Excavation

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Soil excavation is the removal of contaminated soil using heavy machinery such as backhoes and excavators. The excavated soil is either disposed of at a landfill or treated *ex-situ* in a manner appropriate for site-specific purposes.

Advantages of Soil Excavation

- Proven performance; readily available equipment.
- Can achieve significant concentration reduction.
- Short treatment times with quick turn-around, particularly when there are immediate risks to human health, safety, and the environment.
- Can be applied at sites with free product (LNAPL), can be combined with other technologies.
- Under appropriate conditions, soil may be re-used.

Disadvantages of Soil Excavation

- Generally not applicable or cost-effective for sites with contamination deeper than 20 feet bgs (typical reach of excavator arm).
- Significant disturbance to site operations.
- May be costly due to disposal costs of contaminated soil.
- Sometimes not applicable in water-bearing zone depending on the soil type, contaminant mass, and depth of excavation, and groundwater recharge rate.

Application

Remedial soil excavation is effective at removing the majority of impacted soil associated with a petroleum release at a LUFT site, but can be more invasive and can present more challenges than *in-situ* measures for the following reasons:

- Most gas station site soils deeper than 20 feet bgs are not easily removable without shoring due to limited space for lay-back.
- Excavation of soils within the water-bearing zone is logistically challenging and more costly than removing dry soil.
- Excavation requires an area free of surface buildings and subsurface structures.
- Excavation and transportation of excavated soil involve heavy truck traffic and create noise, dust, and often odors and vibrations that may impact the community.
- Excavation may be less cost-effective than many forms of in-situ remediation, and may therefore not be reimbursable by the UST Cleanup Fund if a similarly effective, lower-cost remediation method is available (see the USTCF chapter).

Under some circumstances, however, remedial excavation is the best remediation method available. Conditions which may indicate that excavation is an appropriate remedial technology include:

- Property-related issues, such as redevelopment, which may require rapid, definitive remediation measures.
- Limiting excavation to certain site areas, such as the immediate UST area, to expedite and reinforce other forms of remediation.
- Shallow, soil-only impacts with limited lateral and vertical extent.

- Heavy clay soils (< 3–5% sand or silt) which are unresponsive to other forms of remediation (within 2 to 25 feet of grade). Deeper clayey soils may require other in-situ remediation methods, such as bioremediation, fracturing, heat treatment, etc.

Limits of Excavation

When planning excavation projects, it is most cost-effective to establish the limits of excavation in advance of mobilization and field efforts. The limits can be established in advance by first confirming the numerical remedial goals, and then using existing data or conducting a grid sampling over the impacted area to identify the cells that exceed remedial goals and are to be excavated. The Case Closure Policy requires that free-product (mobile LNAPL) be removed to the maximum extent practicable and that any secondary sources be removed to the extent practicable. Excavation may be an effective means to meet these criteria. Furthermore, the Case Closure Policy defines the concentrations and depths in soil that are protective of the Direct Contact and Outdoor Air pathways (ingestion of soil, dermal contact, and inhalation of volatile or particulate emissions). Additionally, the Case Closure Policy defines the bioattenuation zones that are protective of indoor air. It is possible that excavation of soil to meet these criteria is possible and should be considered when developing the Corrective Action Plan. For further guidance, see the Risk Evaluation and Risk Management chapter.

Soil Remediation Verification

For remedial excavations, “confirmation” or “verification” soil samples are collected from the excavation after the contaminated soil has been removed to verify the effectiveness of the removal. Generally, this is executed by sampling the soil from the sidewalls and at the base of the excavation. If the excavated soil removed is stored onsite, stockpile soil samples will need to be collected and analyzed to determine appropriate soil disposal options. It is advisable to check with the lead regulatory agency prior to conducting such work, because a soil verification sampling work plan may be required if verification soil samples were not conceptually outlined as part of the CAP or are not otherwise specified by local guidance.

Once confirmation soil analytical data are available, the information is compared to criteria in the Case Closure Policy or site-specific remedial goals. In “soils-only” cases, if post-remediation soil concentrations meet the parameters of the Case Closure Policy, or meet site-specific remedial goals, the agency can be requested to approve no further soil remediation. Agency approval is required.

If, however, soil concentrations have *not* been sufficiently reduced, the agency may require additional excavation or a re-evaluation of remedial options and selection of a different remedial solution.

Legal.

According to CCR Title 23, Division 3, Chapter 16, Article 11 §2725, verification monitoring is required to evaluate the effectiveness of the corrective action.

Clean Backfill

Following soil excavation, the area of excavation must be filled with clean backfill. The cleanliness of the fill should be verified by sampling for the COCs and any potential contaminants based on the source of the fill. The RP should contact the lead regulatory agency to determine any local/regional requirements such as the use of certified laboratories, acceptable materials to be used as backfill, COCs to be analyzed in the fill material, compaction requirements, the use of riprap or other fabric barriers, documentation requirements, or any other requirements.

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Remediation in the Unsaturated Zone: Soil-Vapor Extraction

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Soil-vapor extraction (SVE), also known as "soil venting" or "vacuum extraction," is an *in-situ* remediation technology that reduces concentrations of volatile petroleum-hydrocarbon constituents adsorbed to soils in the unsaturated (vadose) zone (EPA 1994).

In this technology, a vacuum is applied to the soil matrix via wells. The reduced pressure due to the vacuum causes these volatile constituents to transform into the vapor phase and move toward the extraction points (i.e., wells). The extracted vapors are then treated as necessary (commonly via carbon adsorption) before being released harmlessly to the atmosphere. The increased air flow through the subsurface can also stimulate biodegradation of some contaminants, especially those that are less volatile.

Drilling Down. The introduction of air into the soil can stimulate indigenous soil bacteria to grow due to the introduction of oxygen, with the result that the bacteria consume substantial quantities of remaining hydrocarbons. The presence of carbon dioxide in the extracted soil vapors is an indicator of bacterial activity. As it normally takes 6 months or more to establish such synergistic bacterial colonies, vapor-extraction processes of shorter duration won't likely show this side effect, or there may be a delay in seeing evidence of colony growth.

Wells may be either vertical or horizontal, although horizontal extraction wells are much more costly than multiple vertical wells and are generally not used at LUFT sites. In areas of high groundwater levels, water-table depression pumps may be required to offset the effect of upwelling induced by the vacuum. One of the best ways to avoid upwelling during SVE is to reduce the applied vacuum.

Advantages of SVE

- Proven performance; readily available equipment; easy installation.
- Minimal disturbance to site operations.
- Shorter treatment times (usually 6 months to 2 years under optimal conditions).
- Cost competitive: $20–$50/ton of contaminated soil.
- Can be applied at sites with free product (LNAPL) and can be easily combined with other technologies.
- Often causes a reduction in groundwater concentrations.

Disadvantages of SVE

- Due to residual petroleum saturation, concentrations reductions greater than 90% of the initial finding are difficult to achieve.
- Effectiveness is less certain when applied to sites with low-permeability soil or stratified soils.
- May require costly treatment for atmospheric discharge of extracted vapors.
- SVE treats only unsaturated-zone soils; other methods may also be needed to treat saturated-zone soils and groundwater.

Application

SVE has been proven effective in reducing concentrations of volatile organic compounds (VOCs) and certain semi-volatile organic compounds (SVOCs) found in petroleum at UST sites. SVE is generally more successful when applied to the lighter (more volatile) petroleum products such as gasoline. Diesel fuel, heating oils, and kerosene, which are less volatile than gasoline, are not readily removed by SVE, nor are lubricating oils, which are non-volatile.

Important! SVE is generally not effective in treating soils below the top of the capillary fringe unless water-table depression pumps are used to draw down the water table. SVE is also generally inappropriate for sites with a groundwater table less than 3 feet bgs. Special considerations must be taken into account for sites with a groundwater table less than 10 feet bgs, because groundwater upwelling can occur within SVE wells under vacuum pressures, potentially occluding well screens and reducing or eliminating vacuum-induced soil vapor flow.

SVE may be appropriate near a building foundation to prevent vapor migration into the building. In this case, the primary goal may be to control vapor migration and not necessarily to remediate soil.

Operating Principles

In SVE, a vacuum is applied to the contaminated soil matrix through extraction wells. This creates a negative pressure gradient, which in turn causes movement of vapors toward these wells. Volatile constituents in the vapor phase are readily removed from the subsurface through the extraction wells. The extracted vapors are then treated (as necessary) and either discharged to the atmosphere or possibly re-injected to the subsurface (if permitted by applicable state laws).

Some of the factors that determine the effectiveness of SVE are:

- Permeability of the soil
- Soil structure and stratification
- Soil moisture content and soil organic content
- Depth to groundwater
- Annual precipitation

The permeability of the soil affects the rate of air and vapor movement through the soil: the higher the permeability of the soil, the faster the movement and (ideally) the greater the volume of vapors available for extraction.

Soil structure and stratification are important to SVE effectiveness, because they can affect how and where soil vapors will flow within the soil matrix under extraction conditions. Therefore, it is important to detail subsurface geology with continuous information to determine structural characteristics (e.g., layering, fractures) can result in preferential flow behavior that may lead to ineffective or significantly extended remediation times if these structures are positioned so that the induced air flow does not pass through the area of contamination.

High moisture content in soils can reduce soil permeability, and therefore the effectiveness of SVE, by restricting the flow of air through soil pores. Fine-grained soils create a thicker capillary fringe (increasing moisture content in the soil) than do coarse-grained soils. However, soils which are too dry (moisture content too low) will result in reduced removal rates. In addition, soils with high organic content, similar to too-dry soils, will also have a reduced VOC removal rate.

Definition. **Capillary Fringe** is defined as the area above the water table where water seeps up into the soil via capillary action. The height of the capillary fringe varies with soil porosity and type.

System Design

Design radius of influence (ROI) is the most important parameter to be considered in the design of an SVE system. The ROI is defined as the greatest distance from an extraction well at which a sufficient vacuum and vapor flow can be induced to adequately enhance volatilization and extraction of contaminants from the soil. Extraction wells should be placed so that the overlap in their ROIs completely covers the area of contamination.

Fluctuations in the groundwater table should also be considered when designing an SVE system. Significant seasonal or daily (tidal or precipitation-related) fluctuations may, at times, submerge some of the contaminated soil or a portion of the extraction well screen, making it unavailable for air flow. This is most important for horizontal extraction wells, where the screen is parallel to the water-table surface.

Surface seals should be included in an SVE system design to prevent surface-water infiltration. They can reduce air-flow rates, reduce emissions of fugitive vapors, prevent vertical short-circuiting of air flow, and/or increase the design ROI. These results are achieved because surface seals force fresh air to be drawn from a greater distance from the extraction well. When surface seals are used, the lower pressure gradients result in decreased flow velocities. These decreased flow velocities may require a higher vacuum to be applied to the extraction wells.

Pilot Testing

Pilot studies are an important part of the design phase of a full-scale SVE system. They provide information on the concentration(s) of VOCs likely to be extracted during the early stages of operation of the SVE system and evaluate the effectiveness of an SVE design.

Pilot studies typically include short-term (1 to 30 days) extraction of soil vapors from a single extraction well, which may be an existing monitoring well at the site. Longer-term pilot studies (up to 6 months) which utilize more than one extraction well may be appropriate for sites with more widely spread contamination.

In some instances, it may be appropriate to evaluate the potential of SVE effectiveness using a screening model such as HyperVentilate (EPA 1993). HyperVentilate can be used to identify required site data, decide whether SVE is appropriate at a site, evaluate air permeability tests, and estimate the minimum number of wells needed. It is not intended to be a detailed, SVE-predictive modeling or design tool.

Pilot Testing Considerations and Preparations

Well(s) to be used during the pilot test are installed in close proximity to the source area undergoing remediation. The well screen and filter pack are, in most cases, no longer than 10 feet to avoid friction loss. Wells are located in the vadose zone or capillary fringe, above the equilibrated groundwater level, to avoid pulling water over the screen (no vapor flow will occur under these circumstances). To maximize flow, extraction wells typically have a larger screen slot size and/or a sand filter particle size than those normally used for a groundwater monitoring well.

It may be appropriate to use a groundwater monitoring well for test purposes if it has a screen interval extending 5 feet or more above the top of the equilibrated water level.

To provide the most flexibility during the test, observation well(s) should be spaced between 10 and 20 feet from the extraction point. If wells are too far away, vacuum changes will not be observed. Most soil types exhibit extraction ROIs ranging from 5–10 feet (clays) to 40–50 feet (sands) at moderate extraction rates (100–250 cubic feet per minute [cfm]). If the test shows no response from wells at a distance of 10–20 feet from the extraction point, either there are construction problems with one or more wells, the test has been conducted incorrectly (for example, too much vacuum has been applied, resulting in upwelling water sealing off the extraction well screen), or the soil is too impermeable for vapor extraction to be an effective remediation measure.

Soils containing a high percentage of clay usually do not respond well to SVE, but any percentage of silts, sands, or gravels generally increases the ability of the soil to be vented. One extraction well and one to two observation wells are minimal requirements for short-term tests.

If soil types vary significantly laterally and/or vertically across the site, more extraction and/or observation wells may be needed to get an idea of potential vapor flow patterns.

Ideally, observation wells should be screened in at least part of the same depth interval as the extraction well(s), unless the soil types are more permeable (i.e., mostly sandy or gravelly), or if clay/silt lenses are laterally discontinuous ("pinch out") between the areas where the injection and observation wells are located.

Pilot Testing Procedure

Prior to test start-up, identify wells and equipment monitoring points. During the initial test start-up, record separate baseline vapor monitor concentrations, air flow rate, vacuum, temperature, humidity, screen interval, and depth-to-water measurements (field data) for each extraction and observation well. Influent air manifold and wellhead equipment should allow for concurrent reporting of isolated field data measurements from individual extraction wells.

Tighten piping, hose connections, and seals to prevent leaks. Vacuum is then applied to the extraction wells at two or three different levels, starting with the lowest possible applied vacuum. During the test, field data from the test wells are recorded at specified intervals proposed in the work plan. Monitoring can range from every 30 seconds to once every 30 minutes or more.

Samples may be collected into vapor sampling containers for laboratory analysis at periodic intervals in order to confirm that field sampling is accurate. These samples are generally collected less frequently than samples taken with field monitors (for example, once at the beginning, middle, and endpoint of the test).

Observation well pressure gauges are checked for changes throughout the test, usually before starting the test, and before and after changing the applied vacuum.

Data Analysis and Interpretation

There are many mathematical models to determine the ROI based on laminar flow equations. Studies (DiGiulio 1992, EPA 2001) have identified a general rule of thumb that can be used for SVE system design purposes: 0.1 inch of water vacuum is the minimum level required to induce vapor flow. In practice, 0.2 inch of water vacuum is a more conservative value.

This means that if, during a test, an observation well does not show at least 0.1–0.2 inch of water response, and the applied vacuum is the highest that can be applied without drawing water over the extraction well screen, then the ROI is less than the distance between the extraction and the observation well(s).

Remediation Application

At sites where soil types are not uniform (that is, they vary laterally and vertically), the ROI may be similarly variable. Ideally, the ROI in uniform formations translates to a circular area of influence when drawn on a plan-view site map. Non-uniform soils create non-circular areas of influence. In cross-section, the area of influence extends upward from the point of extraction in a cone shape.

Reviewing extraction test results while simultaneously viewing a cross-section can often help with interpretation. Clay soils may have an ROI of <5 feet to >10 feet, depending on the amount of silt or sand present. Silts tend to have an ROI of 15 to 25 feet, and sands can have an ROI of 40 feet or more. As soils dry due to repeated exposure to air, the ROI influence can change over time.

Spacing wells slightly closer together than the 0.1 inch of water vacuum response predicts may help prevent zones from forming between wells where the induced vacuum is too weak to create the desired remediation effect. Spacing wells too closely, however, can be inefficient and cost-**in**effective.

Where different soil types exist, multiple source zones extending over large vertical distances may necessitate the installation of several extraction wells screened at varying vertical elevations. Well-screen slot size and filter pack should be designed to ensure optimal contaminant removal for specific soil types, because the vapor flow will follow the path of least resistance.

For Example, a vapor-extraction well that is screened across both sand and clay soils will remediate only the sand, leaving the clay largely as-is.

Wells to address different soil types can be installed as “clusters” (separate wells near each other) or as “nested” wells (differently constructed wells in the same borehole). Local agencies may have regulations restricting or preventing nested-well construction.

The seal on the top of the filter pack should be of sufficient thickness and installed so as to prevent leaks. Multiple source zones extending over large vertical distances and/or zones of low permeability may necessitate the installation of several extraction wells screened at varying vertical elevations.

During sustained extraction (full-scale implementation), sandy/gravelly soils will usually show high levels of vapor removal at first with relatively quick declines in concentrations due to low adsorptive capacity and the relatively high permeability of the soil. Silty/clayey soils have different grain structures and permeability characteristics, and usually show more gradual changes in extracted vapor concentrations over time.

Vapor Treatment

Catalytic/thermal oxidizers are more cost-effective at higher extracted vapor levels (i.e., 3–5% or more of the Lower Explosive Limit [LEL]), while granular activated carbon systems are more cost-effective at lower extracted vapor levels (1-2% LEL). Oxidizers incinerate off-gas, while carbon systems adsorb vapors and must be replaced when saturated.

Sites with mixed soil types may require sequential pieces of equipment. For example, an oxidizer may be appropriate for several months after startup while sandy strata are being treated (high rates of vapor generation), followed by transition to carbon later in the remediation process to remediate silts and clays with lower off-gassing rates.

Further Reading.

Variations and/or enhanced test procedures are available from a variety of sources, including EPA's *Development of Recommendations and Methods to Support Assessment of Soil Venting Performance and Closure*. EPA/600/R-01/070. September 2001.

Rebound Testing

Rebound testing is used to determine whether the SVE system has reached its performance limit, and is normally conducted before collection of soil verification samples.

For soil remediation, stabilization of extracted vapor levels is verified by "pulsing" (turning the system on and off for a certain period of time) to check for "rebound" (increased concentrations after a period of system dormancy). If, after restarting, extracted vapor levels show concentrations at or near the levels observed before shutdown, the vapor-extraction process has reached its performance limit.

If concentrations return to levels at or near those observed early in the remediation process, then the system is usually re-started and operated for a brief period (for example, 1 to 4 weeks) and then shut down again for further rebound testing. If, after several such cycles, the concentrations fail to stabilize at levels close to those observed before the shutdown series began, additional evaluation of the remediation method or specific application (i.e., number and screening of extraction wells) may be appropriate. If the concentrations after the "off" cycle are near or less than the concentrations before the shutdown, the regulatory agency can be requested to evaluate removal of the remediation system.

Due to low rates of adsorption and because most of the hydrocarbon mass is removed during the advective stage, sandy soils usually show no to low rebound effects, while silty/clayey soils may require extensive pulsing to attain stable minimum levels. Clayey/silty soils often show rebound due to slower rates of desorption because of the dominance of diffusional processes in low-permeability soils.

The completion of groundwater extraction remediation is largely evidenced by declining concentrations of COCs in the groundwater plume. For groundwater extraction processes, "rebound" testing can consist of turning the system off over a period of months to see whether concentrations remain at stable, low levels, or if they increase.

General remediation rebound testing, where groundwater has been affected, consists of a pre-determined, post-remediation groundwater monitoring period. The regulatory agency determines this period, usually between 6 months and 1 year. Parameters to be analyzed during the post-remediation monitoring period usually are limited to primary COCs. An extended period of post-remedial monitoring may be required for sites in close proximity to receptors.

If post-remediation groundwater concentrations remain stable at or near those observed when remediation was halted for the duration of the post-remediation monitoring period, the agency can be requested to evaluate for closure. If groundwater concentrations "rebound" to levels near those at the start of remediation or to levels above approved closure goals during the post-remediation monitoring period, these data can be submitted to the agency with recommendations for the next required steps.

Definition: **Significant Rebound** is a relative term. If an SVE system started operations at 5,000 parts per million by volume [ppm(v)] and, prior to shutdown, extracted concentrations declined to 50 ppm(v), a "significant rebound" might be post-shutdown levels of 300 to 500 ppm(v). However, if pre-remediation groundwater concentrations were at a maximum of 13,000 micrograms per liter (µg/L) of MTBE, which declined to 300 µg/L MTBE and then "rebounded" to 400 µg/L MTBE, this might not be evidence of true rebound.

Rebound considerations are also dependent on site-specific factors, such as risk and receptor setting, pre- and post-remediation conditions, etc.

Based on verification testing completed to regulatory specification, if concentrations show declines below agency-approved closure goals, the agency will most likely close the case.

If, however, after application of the approved remedial process, concentrations have declined but are still above remediation goals due to limitations of the technology, application, or other factors, this Manual recommends contacting the lead regulatory agency for further guidance. If possible, alternate paths to closure will have been included in the CAP as contingency measures to facilitate their implementation, should the original remedial process prove insufficient to attain closure.

Remediation Completion

Once extracted vapor concentrations have been stabilized, no additional change can be achieved, or the system has reached its performance limit, the general risk that remains needs to be assessed and/or compared to the Case Closure Policy and a determination as to whether additional soil remediation is necessary made. Removal of the majority of the hydrocarbon plume in soil often sufficiently reduces the risk to groundwater and/or potential receptors such that no further remediation is necessary. Post-remediation soil concentrations can be evaluated by collecting soil samples in the former area of highest concentrations and in areas equidistant from remediation extraction wells.

Further Reading.

The text in this chapter is an excerpt from the publication by the Office of Underground Storage Tanks (OUST), "How to Evaluate Alternative Cleanup Technologies for UST Sites: A Guide for Corrective Action Plan Reviewers" (EPA 1994). This publication provides extensive detail on technologies for remediation of petroleum releases. http://www.epa.gov/swerust1/pubs/tums.htm

Chapter 18: Remediation

Remediation in the Unsaturated Zone: Bioventing

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Bioventing is an *in-situ* remediation technology that uses indigenous microorganisms to biodegrade organic constituents adsorbed onto soils in the unsaturated zone. Soils in the capillary fringe and the saturated zone are not affected. Through bioventing, the activity of indigenous bacteria is enhanced by inducing air (or oxygen) flow into the unsaturated zone (using extraction or injection wells) and, if necessary, by adding nutrients.

When extraction wells are used for bioventing, the process is similar to SVE. However, while SVE removes constituents primarily through volatilization, bioventing systems promote biodegradation of constituents and minimize volatilization (generally by using lower air-flow rates than SVE does). In practice, some degree of volatilization and biodegradation occurs when either SVE or bioventing is used.

Advantages of Bioventing

- Uses readily available equipment; easy to install.
- Creates minimal disturbance to site operations. Can be used to address inaccessible areas (e.g., under buildings).
- Requires short treatment times: usually 6 months to 2 years under optimal conditions.
- Cost competitive: $45–$140/ton of contaminated soil.
- Easily combinable with other technologies (e.g., air sparging, groundwater extraction). May not require costly off-gas treatment.

Disadvantages of Bioventing

- High constituent concentrations may initially be toxic to microorganisms.
- Not applicable to certain site conditions (e.g., low soil permeabilities, high clay content, insufficient delineation of subsurface conditions).
- Cannot always achieve very low cleanup standards.
- Only treats unsaturated-zone soils; other methods may also be needed to treat saturated-zone soils and groundwater.

Application

All aerobically biodegradable constituents can be treated by bioventing. In particular, bioventing has proven to be very effective in remediating releases of petroleum products including gasoline, jet fuels, kerosene, and diesel fuel. Petroleum products are generally biodegradable regardless of their molecular weight, as long as indigenous microorganisms have an adequate supply of oxygen and nutrients.

Tip: Bioventing is most often used at sites with mid-weight petroleum products (e.g., diesel fuel and jet fuel), because lighter products (e.g., gasoline) tend to volatilize readily and can be removed more rapidly using SVE. Heavier, more stable products (e.g., lubricating oils) generally take longer to biodegrade than lighter products.

Important! Bioventing is not appropriate for sites with groundwater tables less than 3 feet bgs. Special considerations must be taken into account for sites with a groundwater table less than 10 feet bgs, because groundwater upwelling can occur within bioventing wells under vacuum pressures, potentially occluding screens and reducing or eliminating vacuum-induced soil-vapor flow. This potential problem is not encountered if injection wells, instead of extraction wells, are used to induce air flow.

Operation Principles

Soil normally contains large numbers of diverse microorganisms including bacteria, algae, fungi, protozoa, and actinomycetes. In well-aerated soils, which are most appropriate for bioventing, these organisms generally use oxygen to metabolize. Of these organisms, bacteria are the most numerous and active group, particularly at low oxygen levels. Bacteria require a carbon source for cell growth and an energy source to sustain metabolic functions required for growth. Nutrients, including nitrogen and phosphorus, are also required for cell growth.

Hydrocarbon-degrading bacteria use oxygen to metabolize organic material and yield carbon dioxide and water in a process commonly referred to as *aerobic respiration*. The biodegradability (that is, the measure of a constituent's ability to be metabolized by these bacteria) of the constituents present will determine both the rate and the degree at which the constituents will be metabolized by microorganisms. To biodegrade large amounts of petroleum hydrocarbons, a substantial bacterial population is required, which in turn requires oxygen for both the metabolic process and the growth of the bacterial mass itself. Approximately 3 to 3.5 pounds of oxygen are needed to degrade 1 pound of petroleum product.

The permeability of petroleum-contaminated soils will determine the rate at which oxygen can be supplied to hydrocarbon-degrading microorganisms found in the subsurface. In general, the type of soil will determine its permeability. Fine-grained soils (e.g., clays and silts) have lower permeabilities than coarse-grained soils (e.g., sands and gravels). Note that the ability of a soil to transmit air, which is of prime importance to bioventing, is reduced by the presence of soil water, which can block the soil pores and reduce air flow. This is important to consider for fine-grained soils, which tend to retain water.

Soil structure and stratification are important to bioventing because they affect how and where soil vapors will flow within the soil matrix when extracted or injected. Structural characteristics such as micro-fracturing can result in higher permeabilities than expected for certain soils. Increased flow will occur in the fractured but not in the unfractured media (e.g., clay). Stratification of soils with different permeabilities can dramatically increase the lateral flow of soil vapors in more permeable strata, and at the same time reduce the soil-vapor flow through less-permeable strata. This preferential flow behavior can lead to ineffective or extended remediation times for less-permeable strata or to the possible spreading of contamination if injection wells are used.

Note: Bioventing differs from SVE in one fundamental way: the objective is to induce only sufficient air flow to enhance natural biodegradation of the contaminants, but not enough to cause them to volatilize. Air flow may be induced either by extracting soil vapor or injecting atmospheric air. Because of the lower air flow required to achieve bioventing, there is less likelihood than with SVE of causing contaminants to be forced into areas where they could potentially cause problems (e.g., vapor intrusion in basements). For extraction systems, there is usually less of a need for vapor treatment than for SVE systems.

System Design

In general, remediation approaches that rely on biological processes should be subject to field pilot studies to verify and quantify the potential effectiveness of the approach and provide data necessary to design the system. For bioventing, these studies may range in scope and complexity from a simple soil column test or microbial count to field respirometry tests and SVE (or injection) pilot studies. The scope of pilot testing or laboratory studies should be commensurate with the size of the area to be remediated, the reduction in constituent concentration(s) required, and the results of the initial effectiveness screening.

Design ROI is an estimate of the maximum distance from a vapor-extraction (or injection) well at which sufficient air flow can be induced to sustain acceptable degradation rates. Establishing the design ROI is not a trivial task, because it depends on many factors including intrinsic permeability of the soil, soil chemistry, moisture content, and desired remediation time. The ROI should usually be determined through field pilot studies, but can be estimated from air-flow modeling or other empirical methods. Generally, the design ROI can range from 5 feet (for fine-grained soils) to 100 feet (for coarse-grained soils). For sites with stratified geology, ROI should be defined for each soil type. The ROI is important in determining the appropriate number and spacing of extraction or injection wells. Stratified soils may require special consideration in design to ensure that less-permeable strata are adequately vented.

At a site with homogeneous soil conditions, the well should be screened throughout the contaminated zone. The well screen may be placed as deep as the seasonal low water table. A deep well helps to ensure remediation of the greatest amount of soil during seasonal low groundwater conditions.

At a site with stratified soils or lithology, the screened interval can be placed at a depth corresponding to a zone of lower permeability. This placement will help ensure that air passes through this zone rather than merely flowing through adjacent zones of higher permeability.

Air flow is particularly important for soils within the capillary fringe, where a significant portion of the constituents often resides. Fine-grained soils create a thicker capillary fringe than do coarse-grained soils. The thickness of the capillary fringe can usually be determined from soil boring logs (i.e., in the capillary fringe, soils are usually described as moist or wet). The capillary fringe usually extends from one to several feet above the elevation of the groundwater table. Moisture content of soils within the capillary fringe may be too high for effective bioventing. Depression of the water table by groundwater pumping may be necessary to biovent soils within the capillary fringe.

Fluctuations in the groundwater table should also be considered. Significant seasonal or daily (e.g., tidal or precipitation-related) fluctuations may, at times, submerge some of the contaminated soil or a portion of the well screen, making it unavailable for air flow. These fluctuations are most important for horizontal wells, in which screens are placed parallel to the water table surface, as a water-table rise could occlude the entire length of the screen.

Bacteria require moist soil conditions for proper growth. Generally, soils saturated with water prohibit air flow and oxygen delivery to bacteria, while dry soils lack the moisture necessary for bacterial growth. The ideal range for soil moisture is between 40 and 85 percent of the water-holding capacity of the soil. Bioventing promotes dehydration of moist soils by means of increased air flow through the soil, whereas dehydration hinders bioventing performance and extends operation time.

The optimum pH for bacterial growth is approximately 7; the acceptable range for soil pH during bioventing is between 6 and 8. Soils with pH values outside this range prior to bioventing may require pH adjustments prior to and during bioventing operations.

Bacteria require inorganic nutrients such as ammonium (to supply nitrogen) and phosphate (to supply phosphorus) to support cell growth and sustain biodegradation processes. Nutrients may be available in sufficient quantities in site soils but, more frequently, nutrients need to be added via injection to soils to maintain bacterial populations.

Important! The presence of very high concentrations of organic petroleum compounds or heavy metals in site soils can be toxic or inhibit the growth and reproduction of bacteria responsible for biodegradation. However, very low concentrations of organic material will also result in diminished levels of bacterial activity.

Pilot Studies

In order to decide whether bioventing is likely to be highly effective, somewhat effective, or ineffective for site conditions, a pilot study can be performed. Pilot studies or bioventing may range in scope and complexity from a simple soil column test or microbial count to field respirometry tests and SVE (or injection) pilot studies. The scope of pilot testing or laboratory studies should be commensurate with the size of the area to be remediated and the reduction in constituent concentration(s) required. A list and description of commonly used laboratory and pilot-scale studies are provided below.

Soil-Vapor Extraction and Injection Treatability Tests are generally used to determine the ROI that an extraction well or injection well will exert in the surrounding soils, the optimum vapor flow rate and pressure (or vacuum) to be applied to the wells, and the concentration of petroleum constituents in the induced air stream. The test most often includes short-term vapor extraction or air injection from a single well while measuring the pressure effect in monitoring wells or probes spaced at increasing distances from the extraction well or the injection well. The test can assist in determining the spacing, number, and type of wells needed for the full-scale system. It is usually not economically attractive to perform this test for sites with areas smaller than 5,000 cubic yards of *in-situ* contaminated soil or for sites with soil permeabilities greater than 10^{-8} square centimeters (cm^2).

Respirometry Studies are generally used to determine the oxygen transport capacity of the site soils and to estimate the biodegradation rates under field conditions. The test includes short-term injection of an oxygen-inert gas mixture into a well that has been screened in the contaminated soil horizon. Carbon dioxide, inert gas (typically helium), and oxygen concentrations are measured in the injection well and surrounding wells periodically for about 1 to 5 days. The measurements are then compared to baseline concentrations of the gases prior to injection. Increases in carbon dioxide and decreases in oxygen concentrations are indications of biological metabolism of constituents; the inert gas concentration provides the baseline for these calculations. Temperature of the extracted vapor may also be monitored to serve as an additional indicator of biological activities. Field respirometry studies are usually needed only for sites with large areas of contamination, perhaps greater than 100,000 cubic yards of *in-situ* soils requiring remediation, at sites where soil permeability is less than 10^{-8} cm^2, or when reductions of more than 80 percent of the initial concentrations of those COCs with vapor pressures less than 0.5 mm Hg are required.

Laboratory Microbial Screening tests are used to determine the presence of a population of a naturally occurring bacterium that may be capable of degrading petroleum product constituents. Samples of soils from the site are analyzed in an off-site laboratory. Microbial plate counts determine the number of colony forming units (CFU) of heterotrophic bacteria and petroleum-degrading bacteria present per unit mass of dry soil. These tests are relatively inexpensive.

Laboratory Biodegradation Studies can be used to estimate the rate of oxygen delivery and to determine whether the addition of inorganic nutrients is necessary. However, laboratory studies cannot duplicate field conditions, and field tests are more reliable than laboratory studies. There are two kinds of laboratory studies in this context: *slurry studies* and *column studies*.

- Slurry studies, which are more common and less costly, involve the preparation of numerous “soil microcosms” consisting of small samples of site soils mixed into a slurry with site groundwater. The microcosms are divided into several groups. These groups may include control groups that are “poisoned” to destroy any bacteria, non-nutrified test groups that have been provided oxygen but not nutrients, and nutrified test groups which are supplied both oxygen and nutrients. Microcosms from each group are analyzed periodically (usually weekly) for the test period duration (usually 4 to 12 weeks) for bacterial population counts and constituent concentrations. Results of slurry studies should be considered to represent optimal conditions, because slurry microcosms do not consider the effects of limited oxygen delivery or soil heterogeneity.
- Column studies are set up in a similar way, using columns of site soils; they may provide more realistic expectations of bioventing performance.

Further Reading.

The text in this section is an excerpt from OUST’s publication, “How to Evaluate Alternative Cleanup Technologies for UST Sites: A Guide for Corrective Action Plan Reviewers” (EPA 1994). This publication provides extensive detail on technologies for remediation of petroleum releases.

http://www.epa.gov/swerust1/pubs/tums.htm

Chapter 18: Remediation

Remediation in the Saturated Zone: Air Sparging

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Air sparging is a process for treating volatile and/or degradable COCs in groundwater and soil below the water table by the injection of contaminant-free air into the subsurface saturated zone, enabling a phase transfer of hydrocarbons from a dissolved state to a vapor phase. The injected air removes the COCs by volatilization and/or aerobic biodegradation. The volatilized vapors migrate into the vadose zone, where they are removed by vapor extraction or allowed to biodegrade.

The goal of air sparging is to create breakthrough conditions, so that the hydrocarbon mass is transferred from the saturated zone into the vadose zone, where it is then recovered by SVE or undergoes natural attenuation.

Air sparging is not to be confused with in-well aeration, where air is injected using a tube or other device inserted into a monitoring well. In-well aeration has a limited ROI, which is usually confined to the well casing, with little to no penetration into the surrounding water-bearing strata. During air sparging, air forced through the soil column creates “micro-channels” along paths of least resistance.

Pulsed air sparging causes the collapse of the micro-channels as air injection is stopped. The soil-grain packing arrangement is redistributed within the former micro-channel to one of a slightly higher density. When sparging is resumed, new micro-channels are formed in different locations from the former channels. As a result, oxygenated air is more evenly distributed throughout the soil column (more so than continuous sparging) by the individual sparging wells.

There are many pulsed sparging regimens, but common scenarios include operating each sparge well or group of wells in an array for a certain time period (minutes or hours) in sequence while alternating or rotating between individual wells or well groups. The pulsing not only distributes the oxygen as evenly as possible throughout the full 3-dimensional plume area, but also limits mounding (as sparging in any one specific area is temporary), and preferential groundwater gradient flow is less able to be established.

Definition. **Groundwater mounding:** Commonly, an outward and upward expansion of the free water table caused by shallow re-injection, percolation below an impoundment, or other surface recharge method (essentially, the reverse of the “cone of depression” effect created by a pumping well). Mounding can alter groundwater flow rates and direction; however, the effects are usually localized and may be temporary, depending upon the frequency and duration of the surface recharge events (Alabama State Water Program).

Mounding effects from sparging are temporary and stop when air injection is halted. Mounding occurs because of density differences between sparged and unsparged parts of the soil column, as opposed to actual groundwater elevation differences. Groundwater with air bubbles entrained in it (through the sparging process) has a lower density than unsparged groundwater.

Advantages of Air Sparging

- Readily available equipment; easy installation.
- Implemented with minimal disturbance to site operations.
- Short treatment times (usually less than 1 to 3 years under optimal conditions).
- At about $20–$50/ton of saturated soil, air sparging is less costly than aboveground treatment systems.
- Requires no removal, treatment, storage, or discharge considerations for groundwater.
- Can enhance removal by SVE.

Disadvantages of Air Sparging

- Cannot be used if free product is present (i.e., free product must be removed prior to air sparging).

- Cannot be used for treatment of confined aquifers.
- Stratified soils may cause air sparging to be ineffective.
- Some interactions among complex chemical, physical, and biological processes are not well understood.
- Lack of field and laboratory data to support design considerations.
- Potential for inducing migration of constituents.
- Requires detailed pilot testing and monitoring to ensure vapor control and limit migration.

Application

When used appropriately, air sparging has been found to be effective in reducing concentrations of VOCs found in petroleum products at UST sites. Air sparging is generally more applicable to the lighter gasoline constituents (i.e., light aliphatics), because they readily transfer from the dissolved to the gaseous phase. Air sparging is less applicable to diesel fuel and kerosene. Appropriate use of air sparging may require that it be combined with other remediation methods (e.g., SVE or pump-and-treat). An air-sparging system can use either vertical or horizontal sparge wells. Well orientation should be based on site-specific needs and conditions (EPA 1994).

Air sparging should NOT be used if any of the following site conditions exist:

- Free product is present. Sparging in the presence of NAPL (aka “free product”) results in smearing the product throughout a larger vertical span of the soil column than it otherwise might have occupied, due to the turbulence associated with the sparging process.
- Nearby basements, sewers, or other subsurface confined spaces are present at the site. Potentially dangerous constituent concentrations could accumulate in basements unless a vapor-extraction system is used to control vapor migration.
- Contaminated groundwater is located in a confined aquifer system. Air sparging cannot be used to treat groundwater in a confined aquifer because the injected air would be trapped by the saturated confining layer and could not escape to the unsaturated zone.

Air sparging is most often used together with SVE, but it can also be used with other remediation technologies. When air sparging is combined with SVE, the SVE system creates a negative pressure in the unsaturated zone through a series of extraction wells to control the vapor plume migration. This combined system is called AS/SVE.

Tip. SVE is included with air sparging if the rate of sparging is high enough for air to “breakthrough” into the vadose zone to control vapors. The air that travels into the vadose zone will contain gasoline vapors generated by the mass-transfer process associated with sparging. If the rate of sparging is low enough that air doesn’t breakthrough into the vadose zone, SVE may not be required.

Operation Principles

The effectiveness of air sparging depends primarily on two factors:

- Vapor/dissolved-phase partitioning of the constituents determines the equilibrium distribution of a constituent between the dissolved phase and the vapor phase. Vapor/dissolved phase partitioning is a significant factor in determining the rate at which dissolved constituents can be transferred to the vapor phase (i.e., the mass transfer rate).
- Permeability of the soil determines the rate at which air can be injected into the saturated zone. It is the other significant factor in determining the mass transfer rate of the constituents from the dissolved phase to the vapor phase.

In general, air sparging is more effective for constituents with greater volatility and lower solubility, and for soils with higher permeability. The rate at which the constituent mass will be removed decreases as air-sparging operations proceed and concentrations of dissolved constituents are reduced.

Soil characteristics will also determine the preferred zones of vapor flow in the vadose zone, thereby indicating the ease with which vapors can be controlled and extracted using SVE (if in use).

Stratified or highly variable heterogeneous soils typically create the greatest barriers to air sparging. Both the injected air and the stripped vapors will travel along the paths of least resistance (coarse-grained zones) and could travel a great lateral distance from the injection point. This phenomenon could result in the contaminant-laden sparged vapors migrating outside the vapor-extraction control area.

System Design

The essential goals in designing an air-sparging system are to configure the wells and monitoring points so as to:

- Optimize the influence on the plume, thereby maximizing the removal efficiency of the system.
- Provide optimum monitoring and vapor-extraction points to ensure minimal migration of the vapor/dissolved-phase plume and to prevent undetected migration. In shallow applications, in large plume areas, or in locations under buildings or pavement, horizontal vapor-extraction wells are efficient for controlling vapor migration.

Pilot Testing

Field pilot tests are necessary to adequately design and evaluate any air sparging system. Pilot tests should not, however, be conducted if any of the following conditions are present:

- Free product is known to exist at the groundwater table.
- Vapors can migrate uncontrolled into confined spaces, sewers, or buildings.
- The contaminant source is in a confined aquifer.

The air sparging well(s) used for pilot testing should be located in an area of no more than moderate constituent concentrations. Testing the system in areas of extremely low constituent concentrations may not provide sufficient data and, because sparging can induce migration of constituents, pilot tests are generally not conducted in areas of extremely high constituent concentrations. The air-sparging pilot study should include an SVE pilot study if SVE will be included in the design of the air sparging system (see the SVE Pilot Study section).

The placement and number of air-sparging points required to address the dissolved-phase plume is determined primarily by the permeability and structure of the soil, as these affect the sparging pressure and distribution of air in the saturated zone. Coarse-grained soils (e.g., sand, gravel) have greater intrinsic permeability than fine-grained soils (e.g., clay, silt), and it is easier to move air (and water) through more permeable soil. Greater lateral dispersion of air is likely in fine-grained soils; this can result in lateral displacement of the groundwater and contaminants if groundwater control is not maintained or cannot be maintained.

The ROI is the most important parameter to be considered in the design of the air-sparging system. The ROI is defined as the greatest distance from a sparging well at which sufficient sparging pressure and air flow can be induced to enhance the mass transfer of contaminants from the dissolved phase to the vapor phase. The ROI will help determine the number and spacing of the sparging wells. Air-sparging wells should be placed so that the overlap in their ROIs completely covers the area of contamination.

Tip. Careful evaluation of the ROIs of air-sparging wells and sufficient placement of enough sparging wells to fully overlap the main and downgradient plume areas eliminates the need for additional hydraulic control. In addition, pulsing the air injection and rotating between injection wells, so that no one area receives continual, sustained injection limits mounding effects and can enhance effectiveness.

The sparging air-flow rate required to provide sufficient air flow to enhance mass transfer is site-specific and is determined via pilot testing.

Pilot Testing Procedure

The goal of a pilot test is to determine whether breakthrough conditions are possible, so that the hydrocarbon mass can be transferred from the saturated zone into the vadose zone, where it is then recovered by SVE.

Detection of increased levels of hydrocarbon vapors in the observation wells compared to pre-test conditions is evidence of breakthrough.

Pilot tests should include the installation of a single sparging point, several vapor-extraction points (if SVE is to be included in the design), and soil-gas monitoring points to evaluate vapor generation rates and to define the vapor plume. Existing groundwater monitoring wells (normally not fewer than three to five wells around the plume) that have been screened above the saturated zone and through the dissolved-phase plume can be used to monitor both dissolved and vapor phase migration, to monitor for changes in dissolved oxygen, and to measure changes in the depth to the groundwater table surface. Additional vapor probes should be used to further define the vapor plume and identify any preferential migration pathways.

If SVE is to be used in the air sparging system, the first portion of the test should be conducted using vapor extraction only, without the air-sparging system being operated. This portion of the pilot test will establish the baseline vapor-extraction levels, the extent of the non-sparged vapor plume, the SVE well ROI, and the intrinsic permeability of the unsaturated zone. The air sparging portion of the test should be conducted with the sparging point operating at variable sparge pressures (e.g., 5 pounds per square inch-gauge [psig], 10 psig) and different depths (e.g., 5 feet, 10 feet below the dissolved-phase plume). It is essential that vapor equilibrium be obtained prior to changing the sparge rate or depth. When no change in vapor emission rates from baseline occurs, the air sparging system may not be controlling the sparge-vapor plume, possibly due to soil heterogeneity. Assess the potential for this problem by reviewing the site's soil lithology. During this test, the hydraulic gradient and VOC concentrations in soil vapors extracted from monitoring wells must be monitored until equilibrium is reached.

The final portion of the pilot test is the concurrent operation of the SVE pilot system and the air sparging system, if applicable. This portion of the test will determine the optimum SVE system (i.e., the number and orientation of wells) that will capture the sparged VOCs for various sparging rates. In addition, this portion of the test requires monitoring of VOC emissions, sparging pressure and flow rates, SVE vacuum and flow rates, monitoring-well vapor concentrations, and dissolved constituent concentrations (EPA 1994).

Data Interpretation

Tips. Be aware of these common air-sparging issues:

- Insufficient injection rates to attain breakthrough.
- Design parameters fail to account for the radius of vapor extraction being insufficient to capture the sparged vapors (e.g., not enough vapor-extraction wells or wells spaced too far apart, incorrectly constructed too high in the vadose zone, etc.).
- Sparge wells screened in zones with too-low permeability (sparging cannot occur) or screened too high in the aquifer (deeper plume components at the base of the aquifer will not be remediated by the sparging process).
- Vadose zone is substantially less permeable than the sparged depth interval – vapors will not be able to break through, and the plume is forced laterally outwards.
- Silty soils overlying sands may experience delayed breakthrough or the site may have a relatively large ROI of air sparging, but if the permeability difference is too great, breakthrough never occurs and the plume channels/spreads downgradient.

Increased vapor concentrations and/or dissolved oxygen (DO) levels in observation wells after test initiation are evidence that the ROI includes the observation well. Measuring the ROI on a basic level consists of extrapolating data based on the distance between the injection and observation wells. For example, if the observation well is 15 feet from the injection well and vapors are observed in the well after initiating the test, the ROI is at least 15 feet. Various software programs and/or calculations can be used to determine more precisely the expected lateral ROI.

Interpretation of the ROI includes consideration of lithologic heterogeneity and the potential for air to flow through preferential migration pathways. Sands tend to have a smaller ROI than silts and clays due to increased permeability; that is, injection meets with less resistance. The ROI of air sparging is inversely proportional to increases in permeability, whereas the radius of vapor-extraction influence is directly proportional to increases in permeability. The limitations of both technologies are met in clay soils, which have very small ROIs to vapor extraction, and are very difficult to sparge without artificially increasing permeability, except at very low flow rates.

The vertical radius of sparge influence is an inverted "V" upwards from the tip of the sparge point, which diminishes upwardly, proportional to the friction loss experienced with relation to the soil type. A thick zone requiring treatment may require sparge well clusters installed to various depths to best treat the entire vertical extent of the plume.

Remediation Application

The combined sparge ROI should fit within the combined radius of vapor-extraction influence to prevent sparged vapors escaping effective capture. The rate of SVE must be sufficient to capture all of the sparged vapors.

While vapor extraction will be constant during air injection in order to contain the sparged vapors, pulsing air injection takes advantage of soil-grain packing and soil mechanics, and substantially increases the effectiveness of the sparging process.

Injection of air creates temporary flow pathways in the soil, changing the grain-packing structure such that grains are closer together during the time air is passing through the flow pathway. Once sparging is stopped, the air channels collapse, forming a less-permeable structure in the soil. The next time air is injected, the air, following the path of least resistance, creates a new flow pathway in a different part of the subsurface.

Utilizing repeated pulsing, the overall surface area of soil exposed to the sparging process is exponentially increased, whereas sustained injection without pulsing simply transports the air through a single set of flow pathways. Pulsing therefore dramatically increases the efficiency of air sparging. Pulse timing is lithology-dependent, but can range from a few minutes per event to several hours. Full-scale application may involve pulsing each injection well in turn (higher per-well injection pressures) or pulsing all wells at the same time for a specified duration (more areal coverage, but lower injection pressure per well point).

Further Reading.

The text in this section is an excerpt from OUST's publication, "How to Evaluate Alternative Cleanup Technologies for Underground Storage Tank Sites: A Guide for Corrective Action Plan Reviewers" (EPA 1994). This publication provides extensive detail on technologies for remediation of petroleum releases.

http://www.epa.gov/swerust1/pubs/tums.htm

Chapter 18: Remediation
Remediation in the Saturated Zone:Biosparging

September 2012

Biosparging is an *in-situ* groundwater remediation technology that uses indigenous microorganisms to biodegrade organic constituents in the saturated zone. Through biosparging, air (or oxygen) and nutrients (if needed) are injected into the saturated zone to increase the biological activity of the indigenous microorganisms. Biosparging can be used to reduce concentrations of petroleum constituents that are dissolved in groundwater, adsorbed to soil below the water table, and within the capillary fringe. Although constituents adsorbed to soils in the unsaturated zone can also be treated by biosparging, bioventing is typically more effective for this situation.

When volatile constituents are present, biosparging is often combined with SVE or bioventing and can also be used with other remediation technologies. When biosparging is combined with vapor extraction, the vapor-extraction system creates a negative pressure in the vadose zone through a series of extraction wells that control the vapor plume migration.

Advantages of Biosparging

- Readily available equipment; easy installation.
- Implemented with minimal disturbance to site operations.
- Short treatment times, 6 months to 2 years, under optimal conditions.
- Cost competitive.
- Enhances the effectiveness of air sparging for treating a wider range of petroleum hydrocarbons.
- Requires no removal, treatment, storage, or discharge of groundwater.
- Low air-injection rates minimize potential need for vapor capture and treatment.

Disadvantages of Biosparging

- Can only be used in environments where air sparging is suitable (i.e., uniform and permeable soils, unconfined aquifer, no free-phase hydrocarbons, no nearby subsurface confined spaces).
- Some interactions among complex chemical, physical, and biological processes are not well understood.
- Lack of field and laboratory data to support design considerations.
- Potential for inducing migration of constituents.

Application

When used appropriately, biosparging is effective in reducing concentrations of petroleum products at UST sites. Biosparging is most often used at sites with mid-weight petroleum products (e.g., diesel fuel, jet fuel); lighter petroleum products (e.g., gasoline) tend to volatilize readily and to be removed more rapidly using air sparging. Heavier products (e.g., lubricating oils) generally take longer to biodegrade than lighter products, but biosparging can still be used at these sites.

The existing literature contains case histories describing both the success and failure of biosparging; however, since the technology is relatively new, there are few cases with substantial documentation of performance.

Operation Principles

The biosparging process is similar to air sparging. However, while air sparging removes constituents primarily through volatilization, biosparging promotes biodegradation of constituents rather than volatilization (generally by using lower flow rates than are used in air sparging). In practice, some degree of volatilization and biodegradation occurs when either air sparging or biosparging is used.

The effectiveness of biosparging depends primarily on two factors:

- The permeability of the soil, which determines the rate at which oxygen can be supplied to the hydrocarbon-degrading microorganisms in the subsurface.
- The biodegradability of the petroleum constituents, which determines both the rate at which and the degree to which the constituents will be degraded by microorganisms.

In general, the type of soil and porosity will determine its permeability. Fine-grained soils (e.g., clays and silts) have lower permeabilities than coarse-grained soils (e.g., sands and gravels). More-permeable soils allow for easier air flow.

Bacteria require a carbon source for cell growth and an energy source to sustain metabolic functions required for growth. The biodegradability of a petroleum constituent is a measure of how well it can be metabolized by hydrocarbon-degrading bacteria or other microorganisms. Petroleum constituents are generally biodegradable, regardless of their molecular weight, as long as indigenous microorganisms have an adequate supply of oxygen and nutrients. For heavier constituents (which are generally less volatile and less soluble than lighter constituents), biodegradation will exceed volatilization as the primary removal mechanism, even though biodegradation is generally slower for heavier constituents than for lighter constituents.

The presence of very high concentrations of petroleum organics or heavy metals in site soils can be toxic or inhibit the growth and reproduction of bacteria responsible for biodegradation. Conversely, very low concentrations of organic material will result in diminished levels of microbial activity.

Other factors that influence the efficacy of biosparging are those that affect the growth and viability of the microorganisms which degrade petroleum hydrocarbons. These factors include:

- Temperature of the groundwater
- pH levels
- Presence of sufficient electron acceptors
- Nutrient concentrations

Bacterial growth rate is a function of temperature. Microbial activity has been shown to significantly decrease at temperatures below 10°C. The microbial activity of most bacteria important to petroleum hydrocarbon biodegradation also diminishes at temperatures greater than 45°C. Within the range of 10°C to 45°C, the rate of microbial activity typically doubles for every 10°C rise in temperature.

To support bacterial growth, the pH should be within the 6 to 8 range, with a value of about 7 (neutral) being optimal. If the groundwater pH is outside this range, it is possible to adjust the pH prior to and during biosparging operations. However, pH adjustment is often not cost-effective, because the natural buffering capacity of the groundwater system generally necessitates continuous adjustment and monitoring throughout the biosparging operation. In addition, efforts to adjust pH may lead to rapid changes in pH, which are also detrimental to bacterial activity.

For biosparging applications directed at petroleum products, bacteria that use oxygen as an electron acceptor (that is, they metabolize organic contaminants aerobically) are most important in the degradation process, because they can degrade these products more rapidly than organisms which use other electron acceptors. The rate of biodegradation will depend, in part, on the supply of oxygen to the contaminated area, because aerobic metabolism is much faster than anaerobic metabolism. When there is an insufficient amount of dissolved oxygen available, organisms which can use other electron acceptors may degrade the contaminants, but at slower rates.

Bacteria require inorganic nutrients such as nitrogen and phosphate to support cell growth and sustain biodegradation processes. Nutrients may be available in sufficient quantities in the aquifer but, more frequently, nutrients need to be added to maintain adequate bacterial populations. Excessive amounts of certain nutrients (e.g., phosphate and sulfate), however, can repress metabolism.

System Design

There are several factors to consider when designing a biosparge system. The placement and number of biosparge points required to aerate the dissolved-phase plume is determined primarily by the permeability and structure of the soil, as these affect the sparging pressure and distribution of air in the saturated zone.

The *Bubble Radius* (analogous to the ROI for air-sparging systems) is defined as the greatest distance from a sparging well at which sufficient sparge pressure and air flow can be induced to enhance the biodegradation of contaminants. The bubble radius will determine the number and spacing of the sparging wells. The bubble radius should be determined based on the results of pilot tests. The bubble radius depends primarily on the hydraulic conductivity of the aquifer material in which sparging takes place. Other factors that affect the bubble radius include soil heterogeneities and differences between the lateral and vertical permeability of the soils. Generally, the design bubble radius can range from 5 feet for fine-grained soils to 100 feet for coarse-grained soils.

Important! Biosparging should NOT be used if the following site conditions exist:

- Free product is present. Biosparging can create groundwater mounding, which could potentially cause free product to migrate and contamination to spread.
- Nearby basements, sewers, or other subsurface confined spaces are present at the site. Potentially dangerous constituent concentrations could accumulate in basements unless a vapor-extraction system is used to control vapor migration.
- Contaminated groundwater is located in a confined aquifer system. Biosparging cannot be used to treat groundwater in a confined aquifer because the injected air would be trapped by the saturated confining layer and could not escape to the unsaturated zone.

The *Sparging Air Flow Rate* required to provide sufficient air flow to enhance biological activity is site-specific and will be determined via the pilot test. Typical air-flow rates are much lower than for air sparging, ranging from 3 to 25 standard cubic feet per minute (scfm) per injection well. Pulsing of the air flow (i.e., turning the system on and off at specified intervals) may provide better distribution and mixing of the air in the contaminated saturated zone, thereby allowing for greater contact with the dissolved phase contaminants. If a vapor-extraction system is used, it should have a greater flow capacity and greater area of influence than the biosparging system. Typically, the SVE rates range from 1.25 to 5 times greater than the biosparging rate.

The *Sparging Air Pressure* is the pressure at which air is injected below the water table. Injection of air below the water table requires pressure greater than the static water pressure (1 psig for every 2.3 ft of hydraulic head) and the head necessary to overcome capillary forces of the water in the soil pores near the injection point. A typical system will be operated at approximately 10 to 15 psig. Excessive pressure may cause fracturing of the soils and create permanent air channels that can significantly reduce biosparging effectiveness.

The *Nutrient Formulation and Delivery Rate* (if needed) will be based on the results of the laboratory tests and pilot study results. Common nutrient additions include nitrogen (in an aqueous solution containing ammonium ions) and phosphorus (in an aqueous solution containing phosphate ions). Note that state regulations may either require permits for nutrient injection or prohibit them entirely.

The *Initial Constituent Concentrations* will be measured during pilot-scale studies. They establish a baseline for estimating the constituent mass removal rate and the system operation time requirements. In addition, they will help to determine whether vapor treatment will be required.

The *Initial Concentrations of Oxygen and* CO_2 in the saturated zone will be measured during pilot studies. They are used to establish system operating requirements, to provide baseline levels of subsurface biological activity, and to allow measurement of the system's progress.

Further Reading.

The text in this section is an excerpt from OUST's publication, "How to Evaluate Alternative Cleanup Technologies for Underground Storage Tank Sites: A Guide for Corrective Action Plan Reviewers" (EPA 1994). This publication provides extensive detail on technologies for remediation of petroleum releases.

http://www.epa.gov/swerust1/pubs/tums.htm

Chapter 18: Remediation

Remediation in the Saturated Zone:In-Situ Chemical Oxidation

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In-situ chemical oxidation (ISCO) involves the introduction of a chemical oxidant into the subsurface for the purpose of transforming groundwater or soil contaminants into less harmful chemical compounds. The process enhances mass transfer and has been used successfully at both existing and newly discovered environmental sites. ISCO is specifically used to reduce contaminant mass and concentrations in soil and groundwater, contaminant mass flux from source areas to downgradient pump-and-treat systems, and to reduce anticipated cleanup times required for natural attenuation and other remedial options (EPA 2006.

The four most common oxidants and their respective reactions are provided below (EPA 2006):

- Permanganate (MnO_4^-)
- Fenton's reagent (hydrogen peroxide [H_2O_2] and Ferrous iron [Fe^{+2}]) or catalyzed hydrogen peroxide (CHP)
- Ozone (O_3)
- Persulfate ($S_2O_8^{2-}$)

Oxidant and Reactions	Electron Potential (E_h)
Permanganate	
$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2\ H_2O$	1.7 V (permanganate ion)
Fenton's Reagent (H_2O_2 derived reactants)	
$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	1.8 V (hydrogen peroxide)
$2\cdot OH^- + 2H^+ + 2e^- \rightarrow 2H_2O$	2.8 V (hydroxyl radical)
$HO_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	1.7 V (perhydroxyl radical)
$O_2^- + 4H^+ + 3e^- \rightarrow 2H_2O$	-2.4 V (superoxide radical)
$HO_2^- + H_2O + 2e^- \rightarrow 3OH^-$	-0.88 V (hydro-peroxide anion)
Ozone	
$O_3 + 2H^+ + 2e^- \rightarrow O_2 + H_2O$	2.1 V (ozone)
$2O_3 + 3H_2O_2 \rightarrow 4O_2 + 2\cdot OH + 2H_2O$	2.8 V (hydroxyl radical)
Persulfate	
$S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^{2-}$	2.1 V (persulfate)
$SO_4^- + e^- \rightarrow SO_4^{2-}$	2.6 V (sulfate radical)

Because ISCO is an emerging technology, the number of laboratory and pilot-scale tests exceeds the number of full-scale deployments. This ratio is improving as this technology is applied and gains acceptance by regulatory agencies and industry. These processes have been used in water and wastewater treatment plants worldwide for many years; however, the environments in which they have been used is 100-percent controlled. Subsurface implementation involves many unknown parameters, some which could possibly cause unforeseen new environmental hazards. For this reason, ISCO methods may take time before full-scale use is commonplace.

Bioremediation vs. ISCO? **Bioremediation** involves bio-chemcial processes to reduce target compound concentrations using microbes in both aerobic and anaerobic environments in-situ and above ground. **ISCO** technologies use physical-chemical oxidation processes to reduce target compound concentrations by addition of high concentrations of oxidants in-situ.

Advantages of ISCO

Much of the technical background for the advantages and disadvantages for ISCO has been drawn from EPA 2004 and EPA 2006.

- Contaminant mass can be reduced *in-situ*.
- Rapid destruction/degradation of contaminants (measurable reductions in weeks or months).
- Produces minimal to no significant waste by-product.
- Vapor-phase volatile organic compound off-gassing is minimal, except for Fenton’s Reagent.
- Some of the oxidants, with the exception of Fenton’s Reagent, are capable of completely oxidizing methyl tertiary butyl ether (MTBE) (but production of degradation products may be problematic).
- Reduced operation, maintenance, and monitoring effort and cost.
- Compatible with post-treatment natural attenuation and can even enhance aerobic and anaerobic biodegradation of residual hydrocarbons.
- Some oxidation technologies cause only minimal disturbance to site operations.

Disadvantages of ISCO

- Potentially higher initial and overall cost relative to other source area remediation technologies, though this is changing with greater use.
- Contamination in low-permeability soils such as clay may not be readily contacted and destroyed by chemical oxidants.
- Contamination in fractured bedrock may not be readily contacted and destroyed by chemical oxidants.
- Fenton’s Reagent can produce a significant quantity of explosive off-gas. Operational precautions are required during implementation of remedial action involving Fenton’s Reagent/hydrogen peroxide.
- Dissolved contaminant concentrations may rebound weeks or months following chemical oxidation treatment.
- Significant health and safety concerns are associated with transporting, handling, and applying oxidants.
- May not be technically or economically able to reduce contaminants to background or regulatory threshold concentrations.
- Subsurface mineralization and other environmental conditions may cause preferential reactions with compounds other than the target contaminants.
- May significantly alter aquifer geochemistry and can cause clogging of aquifer through precipitation of minerals in pore spaces.
- Ozone requires specialized equipment, which may have high-power demands and air permitting requirements.

Application

A brief description of the primary oxidants used for ISCO remediation of petroleum hydrocarbons and related contaminant compounds, and their associated application technologies, is provided below (USEPA 2006).

Table 18-3: Assessment of the Amenability of Various Contaminants and Contaminant Classes to Oxidation Transformations

Contaminant	Oxidant																			
	Permanganate $(MnO4^{-})$				Fenton's Reagent (H_2O_2/Fe)					Persulfate(1) $S_2O_8^{2-}$	Activated Persulfate(1) SO_4^{-}			Ozone (O_3)				Ozone/ H_2O_2 (Peroxone)(2)		
	Source/References (a-e)																			
	a	*b*	*c*	*d*	*a*	*b*	*c*	*d*	*e*	*a*	*a*	*b*	*c*[3]	*a*	*b*	*c*	*d*	*a*	*b*	*e*
Petroleum hydrocarbons	G[4]				E[4]					E[4]	G/E[4]			E[4]				E[4]		
BTEX	P[4]	E[4]	E	E	E[4]	E	E	E	E[4]	E	G[4]	E	E	E						
Benzene	G	G[4]	P[4]	E[4]	E[4]	E	G[4]	G/E[4]	E[4]	E[4]	G[4]	E								
MTBE	E	G	E	E	P/G	E	E	G	E	E	E									
PAHs	G	E	E	E	E	G	G	E	E	G	E	G	G/E	E	G	E	E	G	E	

Key:

P = poor

G = good

E = excellent

While the different sources used slightly different terminology for rating the amenability, in general, they each used a three-tiered ranking represented here by the P, G, and E terminology.

Sources a, e: P = poor, G = good, E = excellent

Source b: P = recalcitrant, G = reluctant, E = amenable

Source c: P = recalcitrant, no/low reactivity; G = reluctant, medium reactivity; E = amenable, high reactivity

Source d: P = difficult to treat, E = susceptible

Notes:

* Modified after Huling and Pivetz, In-Situ Chemical Oxidation, Engineering Issue, EPA/600/R-06/072, August 2006 (USEPA 2006).

1. Persulfate/sulfate radical reactivity studies with 66 organic compounds and isomers under various conditions have been conducted elsewhere (FMC 2005). http://environmental.fmc.com/media/resources/Klozur_Technical_Bulletin_1_-_Activation_Chemistries.pdf.
2. The reaction between O_3 and H_2O_2 produces the hydroxyl ion,·OH. Therefore, the ratings from source (e) by Fenton's (H_2O_2/Fe) apply equally to the O_3/H_2O_2 (Peroxone) technology.
3. Source (c) rated Fe-catalyzed and heat-catalyzed persulfate separately; the lower rating applies to Fe-activated and the higher rating applies to heat-activated persulfate.
4. Benzene was rated separately from TEX or petroleum hydrocarbons; thus, the BTEX or petroleum hydrocarbons rating excludes benzene.

Sources:

a. Sperry, K.L., and J. Cookson, Jr. 2002. In Situ Chemical Oxidation: Design & Implementation. ITRC Presentation to New Jersey Department of Environmental Protection, October 30, 2002. http://www.state.nj.us/dep/srp/training/sessions/insitu200210c.pdf

b. ITRC. 2005. Technical and Regulatory Guidance for In Situ Chemical Oxidation of Contaminated Soil and Groundwater, Second Edition. Interstate Technology and Regulatory Cooperation Work Group, In Situ Chemical Oxidation Work Team.

c. Brown, R.A. 2003. In Situ Chemical Oxidation: Performance, Practice, and Pitfalls. AFCEE Technology Transfer Workshop, February 24-27, 2003, San Antonio, TX. http://www.afcee.af.mil/shared/media/document/AFD-071031-150.pdf

d. Siegrist, R.L., M.A. Urynowicz, O.R. West, M.L. Crimi, and K.S. Lowe. 2001. Principles and Practices of In Situ Chemical Oxidation Using Permanganate. 367 pp. Battelle Press, Columbus, OH.

e. Rating based on the second-order reaction rate constants between contaminants and ·OH reported in Buxton et al. (1988) and Haag and Yao (1992): Excellent (>109 L/mol-s), Good (108 - 109 L/mol-s), Poor (< 108 L/mol-s).

Hydrogen Peroxide and Fenton's Reagent

Hydrogen peroxide is a strong oxidant that can be injected into a contaminated zone to destroy petroleum contaminants. When injected to groundwater, hydrogen peroxide is unstable, and reacts with organic contaminants and subsurface materials. It decomposes to oxygen and water within hours of its introduction into groundwater and generates heat in the process. Peroxide is typically shipped to a remediation site in liquid form at dose concentrations ranging from 5 to 50 percent by weight (EPA 2004).

The reactivity of hydrogen peroxide can limit the extent to which it may be distributed in the subsurface before it decomposes. Injecting concentrations of hydrogen peroxide as low as 100 ppm (a small fraction of one percent) can cause oxygen concentrations in groundwater to exceed the solubility limit of oxygen in groundwater, which is typically 9 to 10 milligrams per liter (mg/L). When this occurs, oxygen is formed, and is lost in the form of bubbles that rise through the saturated zone to the water table and into the unsaturated zone.

Hydrogen peroxide is particularly effective when it reacts with ferrous iron (Fe^{2}+) to produce Fenton's Reagent. Ferrous iron may be naturally present in the subsurface soils and/or groundwater, or it can be added as a catalyst solution together with the hydrogen peroxide to produce this aggressive chemical reaction.

Hydrogen peroxide in the presence of ferrous iron (Fe^{2}+) reacts to form hydroxyl radicals (OH•), ferric iron (Fe^{3}+), and hydroxyl ions (OH-). The hydroxyl ions are very powerful oxidizers, and thoroughly react with organic compounds. The hydroxyl radicals break the petroleum hydrocarbon bonds of common petroleum constituents such as benzene, toluene, ethylbenzene, and xylenes (BTEX) as well as poly-aromatic hydrocarbons (PAHs) and MTBE.

Fenton's Reagent requires soluble Fe^{2}+ to form OH•. This optimal reaction occurs under relatively low pH conditions (e.g., pH of 2 to 4), so a pH adjustment in the treatment area is often necessary to enable the oxidation process to proceed efficiently. This can be accomplished by either acidifying the hydrogen peroxide solution or by adding a chelating acid. Using a ferrous sulfate solution can simultaneously adjust aquifer pH and add the iron catalyst needed for formation of Fenton's Reagent. Because of the low pH requirement, Fenton's Reagent treatment is typically not effective in geologic formations composed of calcium carbonate, such as limestone, or in alkaline sediments with elevated pH levels. In addition, the reaction between hydrogen peroxide and ferric iron can consume hydrogen peroxide, reducing the effectiveness of the oxidant dose. The same effect may also occur in soils with high ferric iron content.

Permanganate

Permanganate is emerging as a chemical oxidant that can be used to destroy petroleum and other organic compounds in soil and groundwater, and has successfully treated MTBE in recent laboratory and bench-scale studies. This oxidant is weaker than hydrogen peroxide. Its inability to oxidize benzene can lead to the early elimination of permanganate as a candidate for oxidation technology at petroleum cleanup sites (EPA 2004); however, since benzene plumes typically do not extend far from the source due to natural attenuation, its use for remediation of MTBE is of more importance.

Permanganate has several advantages over other oxidants. Permanganate:

- Oxidizes organics over a wider pH range.
- Reacts over a prolonged period in the subsurface, allowing the oxidant to more effectively permeate soil and contact adsorbed contaminants.
- Does not normally produce heat, steam, vapors, or other associated health and safety concerns.

Permanganate may be applied to sites as either potassium permanganate ($KMnO_4$) or sodium permanganate ($NaMnO_4$). Where cost dominates over engineering factors at a site, potassium permanganate is the preferred chemical form because it is more widely available, currently costs less, and is available in solid form, which facilitates transport and handling. The liquid form of sodium permanganate is more expensive and difficult to handle and transport, but is more reactive. Sodium permanganate is often applied as a liquid at 40-percent strength, which poses a significant handling and explosion risk.

Ozone

Ozone (O_3) is a strong oxidant with an oxidation potential approximately 1.2 times greater than hydrogen peroxide. Ozone has successfully been used to destroy petroleum hydrocarbons and associated compounds, including *in-situ* MTBE. Ozone, a gas at standard temperature and pressure, is inherently unstable and therefore must be generated onsite. Permitting requirements may require any unused ozone generated on the surface to be destroyed using an ozone destruction chamber to prohibit release into the atmosphere.

Injected ozone dissolves in the groundwater, reacts with subsurface organics, and ultimately decomposes to oxygen. Ozone can oxidize site contaminants directly or through formation of hydroxyl radicals (OH•), strong nonspecific oxidants with an oxidation potential approximately 1.4 times that of ozone. It can oxidize BTEX constituents, PAHs, and MTBE. Peroxone, an ozone-hydrogen peroxide mixture, has shown increased rates of contaminant reduction for MTBE (Mitani et al., 2002).

Ozone and Peroxone Oxidation and Related Chemical Reactions

Direct Oxidation

$3O_3 + C_6H_6 + 3H_2O \rightarrow 6CO_2 + 12H^+$

OH Formation

$O_3 + H_2O \rightarrow O_2 + 2\cdot OH$ (Slow)

$2O_3 + 3H_2O_2 \rightarrow 4\,O_2 + 2\cdot OH + 2H_2O$ (Fast)

Important! Ozone is used in water and wastewater treatment plants worldwide as a substitute for chlorine disinfection. Generation and use is similar to ISCO application, but on a larger scale. Ozone is used in the disinfection process to kill microbes during secondary or tertiary treatment. A by-product of its use as a remediation technology may very likely kill off the microbes responsible for both aerobic and anaerobic contaminant degradation (natural attenuation) in the unsaturated and saturated zone. While this would likely be a temporary condition, the length of time required to restore subsurface conditions to pretreatment state is unknown. Though not investigated in detail, this potential issue should be a consideration during design.

Application

The application of ozone ISCO is a three-step process:

1) Ozone Generation
2) Injection
3) Extraction

Ozone Generation

Ozone is generated using an ozone generator. Ozone is produced in the generator by passing high-voltage electricity through dry air or pure oxygen, or by irradiating the source gas with ultraviolet light. Dry air typically yields 1 percent ozone, while pure oxygen will generate 4 to 10 percent.

Injection

There are two methods of ozone application: injection of gaseous-phase ozone-air mixture, and injection of aqueous-phase ozone mixed with clean water. Gaseous-phase ozone must be pressurized prior to injection. A normal compressor sized for the delivery rate and pressure required can be used. A booster compressor may be required after ozone generation prior to injecting into the sparge-point field. Design considerations for the delivery system must include selection of compatible materials that will not react with ozone or oxidizing environments. Materials such as Teflon™, Viton ™, and 316 stainless steel have been successfully used (EPA 2006).

- **Injection – gaseous phase.** In-situ O_3 oxidation in gaseous form involves the injection of a mixture of outside air and O_3 gas directly into the contaminated unsaturated and/or saturated zones. The mixture is then sparged by injection of air beneath the water table. This promotes volatilization of the contaminant VOCs, ultimately supplies oxygen for later aerobic degradation, and can induce groundwater mixing.

Typically, air containing up to 5 percent ozone is injected into strategically placed sparge wells. Ozone then dissolves in the groundwater, reacts with subsurface organics, and ultimately decomposes into O_2. Ozone oxidizes site contaminants directly and through formation of hydroxyl radicals (OH•), which are strong nonspecific oxidants with an oxidation potential approximately 1.4 times that of ozone. Hydroxyl radicals are capable of oxidizing BTEX constituents, PAHs, and MTBE (with limited effectiveness).

- ***Injection – dissolved (aqueous) phase.*** Ozone can also be injected into the subsurface in a dissolved phase. The gas may be transferred to the dissolved phase onsite by sparging upgradient water with ozone. Upgradient (clean) groundwater is extracted for ozonation and re-injection into the contaminant plume. More commonly, gaseous ozone is injected and sparged directly into contaminated groundwater. Both methods typically require an SVE system to capture vapor-phase VOCs and escaping O_3.

Extraction

SVE is the standard technology used to capture volatile emissions in the unsaturated zone during air sparging and should also be an important consideration and design component for *in-situ* O_3 remediation. Air sparging creates preferential pathways in geologically heterogeneous conditions, typical of most sites, shortly after initial injection. The resulting non-uniform distribution of gaseous ozone and air through limited channels may completely bypass complete sections of contamination. Temporary shut-down and restart of the system will partially eliminate these channels due to settlement. This method is standard practice for non-ozone air sparge systems; however, ozone sparging has a limited timeframe for effective treatment due to relatively quick breakdown of the reactants, or retention time. Several applications over time may need to be considered during design and planning depending on subsurface soil types and other environmental factors.

Persulfate

Persulfate is the newest form of oxidant currently being used for ISCO. Persulfate salts dissociate in aqueous solutions to form the persulfate anion ($S_2O_8^{2-}$). $S_2O_8^{2-}$ is a strong oxidant and can degrade many environmental contaminants, or it can be catalyzed with various reactants to form the sulfate radical (•SO_4^-), a more powerful oxidant. Catalysis of $S_2O_8^{2-}$ to·SO^{4-} can be achieved at elevated temperatures (35 to 40°C), with ferrous iron (Fe^2+), by photo (ultraviolet; UV) activation, with base (i.e., elevated pH), or with H_2O_2. In addition to Fe^2+, other general activators include the ions of copper, silver, manganese, cerium, and cobalt. Persulfate-driven oxidation by SO_4^- has a greater oxidation potential (2.6 V) than $S_2O_8^{2-}$ (2.1 V) and can degrade a wider range of environmental contaminants at faster rates. Formation of·SO_4^- may initiate the formation of OH• and a series of radical propagation and termination chain reactions, where organic compounds can be transformed (EPA 2006).

ISCO System Design

The cleanup goals presented in the CAP answer important questions about the viability of the selected remedial approach and the adequacy of the remedial design. The critical question is, Can the cleanup concentration goals be economically met by the designed chemical oxidation approach? It is important to understand how much oxidant will be consumed and how much will be lost attempting to permeate low permeability soils, in order to weigh the economics and technical feasibility of the approach. Multiple applications of the chemical oxidants may be required in order to accomplish the site objectives (EPA 2004).

Remedial strategies for petroleum UST sites that include a combination of active source zone treatment and enhanced natural attenuation outside the contaminant plume core may consider chemical oxidation technologies. Many chemical oxidation techniques also provide residual dissolved oxygen that is used by aerobic microorganisms to biodegrade contaminants. In addition, these technologies may also oxidize reduced electron acceptors (e.g., nitrogen to nitrate, sulfides to sulfate), which are then used by anaerobic microorganisms to biodegrade contaminants.

Although the design elements of alternative chemical oxidation technologies can vary, some of the following common elements assist with evaluation of the CAP:

- Oxidant Application Design (the oxidant application design should be based primarily on contaminant mass reduction requirements, site characteristics, and cleanup goals)
- Permit requirements and thresholds should be identified in the design so that the system can be constructed to comply with permit requirements and constraints (i.e., permit requirements for injection of chemicals).
- Performance monitoring should be accounted for in the form of a written data quality objective (DQO) plan that can be used to objectively evaluate chemical oxidation system performance.
- Contingency plans should be prepared as part of the remedial design.

Bench-Scale Studies

Objectives

Bench-scale treatability studies can be useful to gain insight on the feasibility of contaminant oxidation prior to pilot- or field-scale applications (EPA 2006). In complex, heterogeneous systems it is difficult to predict specific reactions, oxidation efficiency, oxidation by-products, or whether any of the potential limitations apply. The methods and materials of bench-scale treatability studies may vary based on the oxidant used and the objectives. It is important to recognize the physical differences between bench- and pilot- or field-scale systems. The use of bench-scale treatability results from simplified systems to design field-scale ISCO systems must be closely scrutinized.

Objectives of the bench-scale treatability study are as follows (EPA 2006):

- Establish proof of concept that the target compound can be transformed by oxidative treatment(s), given the potential limitations
- Measure the oxidant demand, which is used to assess the feasibility of ISCO and to assist in the design of oxidant injection at pilot- or field-scale
- Assessment of the reaction by-products, since the oxidative treatment of some target compounds or complex chemical mixtures may be poorly documented or unknown
- Mobilization of redox- and pH-sensitive metals

General Guidelines

Components of the bench-scale reactor should include the aquifer material since it will contain the majority of the contaminant(s) and other parameters that will largely influence oxidant demand and the success or failure of the treatment process (EPA 2006). Disturbed aquifer material is generally used in this procedure. Use of groundwater from the site is ideal but is generally not critical. Capture and quantification of contaminant losses from the reactor is necessary to maintain a mass balance and to assess treatment performance. These losses include volatiles, displacement of aquifer material, aqueous solutions, or DNAPLs. Reactions involving H_2O_2 may release significant quantities of heat and $O_2(g)$ and enhance volatilization. Volatile losses can be captured and quantified using inert gas bags or an activated carbon trap. A nonvolatile contaminant analogue can also be amended to the reaction vessel, and its loss can be used to predict the oxidative transformation of the target compound. Failure to capture volatile losses could result in an overestimate of oxidative treatment.

Pilot Testing

Pilot-scale treatability studies provide useful information to help design and plan full-scale ISCO implementation. Specifically, due to the spatial variability of samples collected and used in bench-scale tests, pilot-scale studies can provide data and information from the oxidative treatment over a larger aquifer volume. The methods and materials of the study may vary based on the oxidant used and the objectives (EPA 2006).

Objectives

The objectives may include the following (EPA 2006):

- Determine the injection rate *vs.* injection pressure

- Assess various injection strategies
- Assess the travel times
- Distribution (vertical/horizontal) and persistence of the oxidant and reagents (Fe, acid, stabilizers, chelators)
- Determine whether groundwater contaminants are mobilized or are volatilized
- Assess the mobilization of metals
- Assess contaminant rebound
- Determine reaction by-products
- Conduct a preliminary performance evaluation of contaminant oxidation
- Assess the adequacy of the monitoring program
- Anticipate well-fouling problems
- Assess the potential difficulties in scaling up a treatment system

Multiple injections of oxidant and/or reagents under different conditions can be used to accomplish different treatment and testing objectives.

General Guidelines

A detailed assessment of ISCO performance evaluation and potential contaminant concentration rebound generally requires extended periods of time due to the slow mass transfer and mass transport processes in conjunction with the slow rate of groundwater movement. Additionally, in Fenton systems, a significant disturbance results from H_2O_2 injection and the subsequent release of heat and O_2(g). It is common to see significant increases in total dissolved solids in groundwater samples collected soon after H_2O_2 injection. Therefore, the groundwater quality is initially degraded due to turbidity and other factors, and requires an extended period of time to approach chemical equilibrium. Both the detailed and general information acquired through the pilot-scale study can be used to help design and plan subsequent injection events. Monitoring data and information are useful to design the monitoring system for the full-scale system including appropriate locations and depths of monitoring wells and appropriate monitoring parameters and frequency.

The following general guidelines for ISCO pilot-scale studies are applicable for all oxidants, and also apply to full-scale implementation. Conceptually, an outside-in injection strategy involves initial oxidant injections on the periphery of the known contaminant zone. Subsequent injections in the middle of the source zone may transport contaminants into adjacent zones already containing oxidant and/or contaminants. Ideally, this reduces the transport of contaminants from the source zone into uncontaminated areas. Groundwater samples represent an integrated measure of contaminants present in the subsurface and provide valuable insight regarding performance evaluation from the oxidative treatment. However, due to the slow mass transfer and mass transport processes which occur in the subsurface, sufficient time should be allowed after ISCO is performed before groundwater samples are collected for performance evaluation. Assuming potential receptors are located close to the injection area, an expedient groundwater monitoring program, including rapid turn-around times for laboratory sample analyses, may be needed.

Pilot- and full-scale ISCO should be implemented in a manner that recognizes and minimizes the transport of contaminated groundwater or LNAPLs from the source area into low contamination/clean areas. Pilot-scale studies are sometimes deployed in or downgradient from a source zone. In this case, it can sometimes be difficult to distinguish between rebound and upgradient flushing of contaminants into the study area. An outside-in approach can be used to help minimize this complication (i.e., a wedge that extends from the upgradient edge to the central area of a source zone). Contaminant transport from upgradient of the remediated area and possible recontamination underscores the need to design the oxidant delivery system for full coverage.

Field-Scale Implementation and Engineering Design Considerations

The treatment objectives for ISCO vary from site to site and include, but are not limited to, the following:

- Reduction in contaminant toxicity, mass, and/or concentration to a risk-based threshold, to maximum concentration levels, or other regulatory limit(s).
- Reduction in contaminant mass flux across a site boundary.

ISCO is a source-depletion technology capable of removing contamination source zones at sites with favorable geologic and hydrogeologic conditions. Achieving drinking-water Maximum Contaminant Levels (MCLs) in these source zones, as well as source zones in more challenging heterogeneous hydrogeologic conditions such as fractured bedrock, karst systems, and multiple stratigraphic units, is unlikely (EPA 2006).

ISCO is often deployed in source areas to minimize long-term sources of groundwater contamination. ISCO has also been deployed at property boundaries for the purpose of preventing off-site migration of groundwater contaminants, and in weathered plumes where NAPL is present in small volumes, or absent altogether. In this scenario, the majority of the contaminants are present as soluble and sorbed phases at lower concentrations compared to source zones. ISCO has also been used to 1 reduce the mass flux to pump-and-treat systems, and 2) reduce the concentration gradient across a low-permeability barrier in hydraulic containment systems. Due to the significant challenges required for ISCO to meet stringent cleanup standards, natural attenuation is an integral component in the overall remedial strategy for both the source zone and downgradient plume.

A single, well-documented, and well-demonstrated oxidant loading and delivery design approach has not been established for any of the listed oxidants. Overall, the state of the science of ISCO involves the combined use of best engineering and scientific judgment (site characterization, feasibility study testing, remedial design, etc.) in conjunction with trial and error. Due to the inherent uncertainty with contaminant distribution, subsurface heterogeneities, and mass transfer/transport mechanisms that occurs at most sites, ISCO requires multiple iterations between oxidant application and performance monitoring. Through this process, clean areas can be identified that require no further treatment, and hot-spot zones can be identified which permit the strategic delivery of additional oxidant to accomplish the treatment objectives.

Data Analysis

The performance of the chemical oxidation system should be evaluated using soil chemistry and groundwater quality data from between, around, and downgradient of oxidant delivery locations rather than inside or in the immediate vicinity of the oxidant delivery points. Conditions inside or in the immediate vicinity of oxidant injection locations have been preferentially altered by chemical oxidation to destroy the petroleum contaminants. Therefore, data from these locations are not representative of the subsurface conditions that exist beneath most of the site.

To understand the effect the chemical oxidation system is having on the subsurface conditions as a measure of its performance, samples of soil, groundwater, and soil gas should be collected from alternate locations. In a review of the performance monitoring plan in the CAP, it is advisable to verify that there are a sufficient number of sampling locations between oxidant application points to provide the necessary performance sampling data. The site characterization parameters needed for ISCO system evaluation are provided in the table below. The sections following provide a description of how these data may be used to evaluate the chemical oxidation system performance.

Table 18-4: Site Characterization Data Needed for ISCO

Parameter	Purpose of the Data/Information
<u>**Target Contaminant**</u> Type(s) Distribution Phase/Concentration	To select which oxidant is most suitable for the specific contaminant(s). To determine where to deliver the oxidant (spatial delivery of the oxidant). Aqueous/sorbed/NAPL — To identify potential hot-spot areas where multiple applications will be required; to estimate contaminant mass, which may be used to estimate the total oxidant mass required.
Geology and Hydrogeology	Estimate rate of oxidant injection based on aquifer hydraulic properties. Information on hydraulic conductivity, gradient and aquifer heterogeneities can be used to identify post-injection flow direction and rates. Assess whether nearby receptors could be impacted.
Aquifer Material/Soil/ Groundwater	Analyzed for organics to quantify and delineate contaminant distribution; used for bench-scale feasibility testing (contaminant oxidation, oxidant demand testing); analyzed for metals to identify hot spot or problematic conditions where pH- or redox-sensitive metals may become mobilized during ISCO.
pH, Buffer Capacity	To assess whether pH modification is needed; acidic pH (3 to 5) is optimal for Fenton oxidation; pH modification will be difficult to achieve in highly buffered soil/aquifer materials; carbonate and bicarbonate buffer species act as radical scavengers in Fenton and persulfate oxidation.
Eh (electrode potential)	General indicator of oxidant demand.
Reduced Inorganics	Soluble metals (Fe(II), Mn(II)), sulfides indicate reducing conditions.

Source: EPA 2006

Evaluation Criteria

The evaluation sampling provides the evidence needed to assess the chemical oxidation system performance. This evidence requires examination and interpretation to confirm chemical oxidation system effectiveness and whether system or application modifications may be warranted. A discussion of these data and how system performance can be interpreted is provided below. In particular, an evaluation of performance is examined from the following two broad chemical oxidation system requirements:

- Oxidant delivery and distribution
- Permanent contaminant mass reduction and attainment of cleanup goal

Each of these is discussed in more detail below.

Oxidant Delivery and Distribution

Performance sampling may indicate that the chemical oxidation system is meeting design specifications for oxidant delivery and distribution if the data show the following:

- Oxidant and catalyst are being delivered to the subsurface at the design mass delivery rate or design adjusted rate based on analysis of field monitoring data; and
- The oxidant and catalyst are detected in samples from the treatment area at the design concentrations.

If the performance monitoring data suggest that one or more of these conditions is not met, the system may not be meeting the requirements of the design, and system adjustments or modifications may need to be made. As previously discussed, the remedial system design should include contingency planning that explores performance deficiency scenarios and identifies possible solutions.

Oxidant delivery deficiencies may be overcome by simply adjusting system flow rates, upgrading equipment capacities, or increasing oxidant dose concentrations. However, occasionally, oxidant delivery rates may be limited by the capacity of the subsurface to transport the delivered oxidant mass.

Perhaps the most challenging performance problem is when a chemical oxidation system or program is unable to deliver oxidants to a portion or multiple portions of a contaminated area. There are many ways that oxidants distributed from delivery points could fail to reach target contaminated area. These may include:

- Low permeability heterogeneous soils.
- Low hydraulic gradient and groundwater flow.
- Possible remedies to the performance problem include adding additional oxidant delivery points; increasing oxidant delivery rates; increasing dose concentrations; or enhancing hydraulic gradients and groundwater flow.

Permanent Contaminant Mass Reduction and Attainment of Cleanup Goal

The effectiveness of a chemical oxidation program can only be determined after examining the reduction in contaminant mass, and after identifying whether the contaminant mass reduction is sufficient for the soil and groundwater to permanently meet cleanup standards.

It is not sufficient to simply review groundwater monitoring data collected during and weeks or even months after completing a chemical oxidation program. These data are often biased, reflecting the successful oxidation of the most readily contacted contaminants, predominantly contaminants in the most permeable soil zones. False-positive evaluations of chemical oxidation program performance can result from reliance on short-term, post-chemical oxidation application groundwater monitoring data. These false positive evaluations may become evident during long-term groundwater monitoring, when contaminant levels rebound as untreated contaminant mass in the less permeable soil bleeds back out and re-contaminates the more permeable zones. In the long term (e.g., months to years), post-chemical oxidation groundwater monitoring is needed to evaluate the effectiveness of a chemical oxidation program.

Program effectiveness may also be evaluated by estimating the mass of contaminants destroyed, which can be accomplished using sample analytical data. Provided that a sufficient number of soil samples are collected and analyzed for the treatment area, soil sampling using identical methods before and after implementation of a chemical oxidation program may indicate the volume of contaminant mass destroyed by the oxidants. Comparing the estimated actual mass destruction with the projected mass destruction (as predicted in the CAP) will reveal the relative effectiveness the oxidant application program. If the contaminant mass destroyed is roughly the amount predicted during the design, the chemical oxidation program can be considered a success.

Further Reading.

The USEPA webpage for ISCO provides a detailed reference list. The webpage can be accessed at:

http://www.epa.gov/ada/gw/isco.html

USEPA document EPA600/R-06/072, “In-Situ Chemical Oxidation” (2006), provides an excellent process fundamentals review, site requirements, and operational and design considerations. This document can be accessed at:

http://www.epa.gov/nrmr/pubs/600r06072.pdf

The Principles of Chemical Oxidation Technology for Remediation of Groundwater and Soil is a commercial design and application manual that provides practical field application knowledge and guidance for use with RegenOx™. This document can be downloaded at:

http://www.regenesis.com/contaminated-site-remediation-products/chemical-oxidation/regenOx/download-manual.aspx

Chapter 18: Remediation
Remediation in the Saturated Zone: In-Situ Groundwater Ozone Sparging

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Ozone (O_3) sparging is an *in-situ* groundwater chemical oxidation technology. This technology is an enhanced form of air sparging which involves the injection of ozone into the groundwater below the water table. The injected ozone migrates outward and upward, causing a chemical oxidation process to take place. As the ozone travels through the saturated zone, the chemical oxidation causes the destruction of LUFT COCs into carbon dioxide (CO_2) and water (H_2O).

Advantages to Ozone Sparging

- Effective in treating MTBE, TBA, and other oxygenates, may be beneficial in treating BTEX when combined with other technologies.
- Can be delivered continuously as opposed to batch applications typically associated with other chemical oxidation techniques, which delivers the opportunity for greater oxidation.
- Ozone is generated onsite, so storage and transportation of dangerous chemicals is not needed.
- Short treatment times.
- Can stimulate biodegradation as an after-effect.

Disadvantages to Ozone Sparging

- Not effective in clays and tight soils.
- Low-flow injection may be insufficient to remediate adsorbed-phase BTEX and TPH below the soil/water interface.
- If trivalent chromium (Cr[III]) is present in the soil in sufficient quantities and/or redox conditions are present, which do not support return to background state outside the immediate area of injection, the possibility of creating hexavalent chromium (Cr[VI]) and/or other by-product species in unacceptable quantities exists.
- Extreme oxidant, which enhances equipment failure and requires technician expertise for safe operations.

Application

When used appropriately, ozone sparging can be effective in reducing concentrations of oxygenate LUFT COCs, including MTBE and TBA, and can be beneficial at degrading BTEX and TPH. Ozone-air sparging destroys dissolved COCs by three key processes. First, when air is bubbled through groundwater in soil pores, dissolved VOCs transfer from liquid to gas phase in accordance with Henry's Law. Second, ozone in the sparge bubbles reacts extremely rapidly with VOCs, destroying them in the process. Thirdly, residual oxygen from the reaction encourages bioremediation, which consumes the breakdown products and converts them to carbon dioxide and water (Schwartz, et al. 2005).

Operational Principles

The use of ozone is different from most oxidation processes: ozone can be injected as a gas. This provides the opportunity to apply the treatment continuously rather than in batch applications. Ozone sparging is best applied at sites with at least moderate soil permeability. Sparging into predominantly clay soils is not likely to be effective unless the permeability is increased artificially by fracturing or other means. Lithology above and below the screened interval of the sparge well influences the outcome as well. Note that the injection of any chemicals may require regulatory permits and it is suggested for the RPs to check with the lead agency prior to remedial activity.

System Design

For groundwater remediation, ozone is transported beneath the groundwater table via injection wells. An air compressor draws in ambient air, which is passed through an oxygen concentrator. The oxygen concentrator removes nitrogen from the air stream and delivers pure oxygen to an ozone generator. The ozone generator uses a high-voltage electrical current to convert oxygen to ozone. Another air compressor is often then used to blend in ambient air with the produced ozone, allowing the ozone to be injected into the subsurface at typical flow rates of 1 to 4 cfm and up to 10 cfm at pressures up to 50 pounds per square inch (psi) and various concentrations of ozone. The mixture of air and ozone is usually injected into the subsurface through micro-porous oxidation points via an oxidation port manifold. A field programmable logic controller (PLC) with an interface panel viewer is used to control the manifold, allowing field personnel to enable and disable oxidation points, switch between ozone and oxygen injection (if the equipment used has this capability), set lag time between sparge cycles, and set sparge duration.

Injection well screens should be located with the base of the well coinciding with the base of the plume. A minimum of 5 feet of groundwater should be present above the top of the injection point's sand filter pack to minimize short-circuiting to the surface. In addition, the bentonite seal should be installed so as to prevent "bridging" (see below). For deeper plumes, several injection wells may have to be installed at progressively shallower depths. The upward vertical limit of sparging is generally between 15 to 20 feet, depending on lithology.

Tip. Injection well construction (typical): 1-inch inner diameter (ID), Schedule 80 Polyvinyl Chloride (PVC) connected to a 1.5-inch diameter by 18-inch-long gas diffuser. Some manufacturers of ozone-generating equipment recommend use of stainless-steel wells and diffusers. If the remediation effort is expected to last more than 5 years, it is recommended that stainless-steel wells be used.

A sand pack of #2/16 or other appropriate sand is placed from the base of the well to at least 1 foot above the top of the gas diffuser, with at least 3 feet of bentonite chips hydrated in place overlying the top of the filter pack. A neat cement grout seal is then placed from the top of the upper bentonite layer to approximately 1 foot below grade. A well-head connection is placed on top of the riser pipe, with an appropriate box set at grade.

In order for ozone sparging to be effective, adequate contact between oxidants and COCs is needed. Accounting for subsurface heterogeneities or preferential flow paths is needed to ensure that there are no pockets of untreated contaminants. Ozone injection points are strategically installed across the area of impact to provide proper overlap of the injection area or ROI. The ROI is usually determined by conducting an ozone sparging pilot test.

Pilot Test

The goal of an ozone sparging pilot test is to inject ozone below the water table and determine whether and how far ozone is migrating through the saturated zone, whether oxidation of COCs is occurring, and to determine the ROI. This is ascertained by installing injection points and monitoring groundwater conditions in adjacent monitoring wells (observation wells).

For pilot-testing purposes, injection test wells should be no more than 15 to 20 feet up- or cross-gradient from at least one nearby groundwater monitoring well (ideally located in the area of highest concentrations). Spacing at greater distances may show no results during the test.

Nearby groundwater monitoring well(s) are used as observation points to evaluate the effects of the test.

Important! It is important to consider that ozone has the potential to oxidize UST tanks, underground lines, or equipment. It is imperative that all components of the system be ozone-compatible, or that ozone injection be conducted sufficiently distant from the fueling system or other underground facilities with which ozone may react. Compatible materials include stainless steel, Teflon, Kynar, Viton, and Schedule 80 PVC. High-density polyethylene (HDPE) and natural rubbers are not compatible and should be avoided.

In addition, measurements of groundwater elevation, pH, oxidation/reduction potential (ORP), electrical conductivity (EC), DO, ambient gasoline-vapor concentrations, and temperature are often collected from both the observation wells and injection wells prior to initiating testing. Changes in these parameters are indicators of chemical oxidation occurring, as discussed in further detail in the "Data Analysis and Interpretation of Pilot Test" section of this chapter.

During initial test start-up, separate baseline DO concentrations, air-flow rate, temperature, and depth-to-water measurements (field data) should be recorded for each injection point and observation well. Screened interval data for new and existing wells should be evaluated prior to the test. Equipment sparge manifold and wellhead equipment should allow for concurrent reporting of isolated field data measurements from individual extraction wells.

Pre-Test Sampling

Before initiating the test, sample the groundwater monitoring wells to be used as observation points for the COCs associated with the site and any by-product species (such as hexavalent chromium and/or bromide/bromate ratios) with the potential to be generated during the test, using standard sampling methods.

Many agencies are concerned with the possible creation of toxic metals such as hexavalent chromium as by-products during oxidant injection; this is discussed in further detail in "Ozone By-Product Evaluation" below. If the site is located in an area where mafic minerals are likely contributors to local soils, or if required by the agency, the following additional pre-test analyses should be considered: manganese, total chromium, vanadium, selenium, and molybdenum by EPA Method 200.8; bromide and bromate by EPA Method 300.1; and hexavalent chromium by EPA Method 7199.

At many sites, hexavalent chromium created as a by-product of ozone injection may be found to be ephemeral and/or limited to the immediate area of injection. Away from the injection point and/or after injection ceases, at these sites the hexavalent chromium will revert back to the trivalent state, as documented by groundwater testing.

Ozone injection can often stimulate biodegradation as an after-effect of the injection process: un-reacted ozone degrades to oxygen. To evaluate the inherent potential of a site to undergo biodegradation related to increased oxygen levels, pre-test sampling should also include testing for the following biodegradation indicators and common natural attenuation parameters: heterotrophic plate count (HPC) (a screening check for aerobic bacterial activity), nitrate, sulfate, ferrous iron (Fe[II]), alkalinity, and specific conductivity.

If biodegradation is desired as a by-product of ozone injection, a one-day test may not show measurable changes; however, the presence of some aerobic bacteria is usually evidence of the potential for the population to increase in response to additional oxygen.

Inorganic compounds and other organic compounds such as chlorinated solvents can increase the amount of ozone needed to destroy LUFT COCs. Inorganic compounds are oxygen receptors which, if present, will create an additional demand on ozone. Chlorinated solvents require larger quantities for complete oxidation to occur than do petroleum hydrocarbons. It is important to understand whether these chemicals are present to determine the amount of ozone needed. If previous data have not been collected for these constituents, groundwater analysis is recommended.

Typical Test Process

During ozone injection, DO and ORP levels are monitored frequently (e.g., every 15 minutes or as practical, based on the number of observation wells being used) in the observation wells, along with depth to water, pH, EC, and temperature. In addition, a PID or FID is used to monitor for the presence of gasoline vapors in the observation wells, and an ozone meter is also recommended to check for the presence of ozone vapors in the observation wells. Such vapors indicate that ozone is migrating in the subsurface from the injection points to the observation wells.

Several different injection pressures should be attempted during a one-day event to obtain a range of data readings, and the various injection pressures recorded as part of the data set. It is not usually desirable to sparge ozone to "breakthrough" pressure (which is conversely the main goal of traditional air-sparging), so the maximum optimal pressure during the test is usually one which is found to be slightly lower than breakthrough. The reason for this is that, once in the vadose zone, ozone vapors require extraction and treatment using SVE equipment, which often reacts negatively to the ozone. Also, breakthrough increases the chances that ozone will migrate to the ground surface, posing issues with surface and atmospheric receptors. During the test, this is accomplished by detecting breakthrough and then reducing the injection pressure. "Breakthrough" is indicated when, as compared with pre-test levels, increased concentrations of either 1) gasoline vapors or 2) gaseous ozone is detected in the observation wells during the test. The presence of gaseous ozone, in particular in the observation wells, is evidence that vapor-phase ozone has "broken through" into the vadose zone from the saturated zone.

DO, ORP, depth to water, pH, EC, and temperature should also be monitored for 2 to 3 hours after the last injection and 24 hours after the last injection. As both DO and ORP meters tend to be very sensitive and lose calibration during the test, calibration of DO and ORP meters is recommended a minimum of two times during the test.

Mobile ozone-injection units are available from various equipment rental companies and/or ozone injection system manufacturers. A typical ozone generator is capable of delivering 1.0 to 20.0 lb of ozone per day, up to 6% concentration by weight, with a variable delivery flow rate between 0.5 and 10 cfm.

Post-Test Analyses

One week after the completion of the ozone injection pilot test, follow-up groundwater samples should be collected from the same observation wells and analyzed for the same suite of constituents as was analyzed in the pre-test sampling.

Tips. Be aware of these common Ozone and/or Oxygen Sparging issues:

- Undersized ozone generator.
- Poor design of ozone delivery system manifold. Does not allow for concurrent reporting of isolated field data measurements from individual extraction wells.
- Poor quality piping and well-head connectors. Piping and connectors exposed to ozone should be corrosion-resistant.
- Sparge wells screened in low-permeability zones or in the wrong part of the water-bearing zone.
- Detecting either gasoline or ozone vapors in observation well(s) during the test indicates that the injection pressure is sufficient to have induced breakthrough. As mentioned in the discussion, this is not desirable.

Data Analysis and Interpretation of Pilot Test

Increased DO and ORP levels in observation wells after test initiation are evidence that the ROI includes the observation well. Measuring the ROI on a basic level consists of extrapolating data based on the distance between the injection and observation wells. For example, if the observation well is 15 feet from the injection well and a DO increase is observed, the ROI is at least 15 feet.

Various software programs and/or calculations can be used to determine more precisely the expected lateral ROI. Interpretation of the ROI includes consideration of lithologic heterogeneity and the potential for ozone to flow through preferential migration pathways.

Conditions that do not support traditional air sparging (such as low-permeability soils overlying high-permeability soils) can support ozone sparging by creating a cap to ozone vapors migrating into the vadose zone.

Decreased dissolved-gasoline concentrations in observation wells or changing ratios of oxygenates indicate that ozone injection has destroyed gasoline within the distance between the injection and observation wells. In particular, MTBE will convert to TBA as a result of partial oxidation. If concentrations of MTBE were higher before the test and TBA was lower, and these ratios reverse, this is evidence of successful (although partial) oxidation.

Sustained injection should result in TBA concentration declines as the reaction is given a chance to break down the TBA.

Ozone By-Product Evaluation

Many regulators are concerned about the creation of by-products such as hexavalent chromium (Cr[VI]) during ozone injection.

There are several risk factors which can predict whether ozone injection at a site will create Cr(VI). The primary risk factor is the presence of significant concentrations of trivalent (Cr[III]) in the soil. If there is no or low Cr(III) in the soil, Cr(VI) will not be created by reactions between site soils and injected ozone.

In addition to the presence of Cr(III), the following site conditions may predispose a site to the creation of Cr(VI) under oxidizing conditions:

- Site location in a sedimentary basin with Franciscan assemblage or similar type source rocks. Soils from these types of rocks are usually rich in both manganese and Cr(III). Manganese is a catalyst for Cr(VI) creation, but is not detectable in groundwater (not soluble). The presence of manganese at a site is determined through soil sampling.
- Low background humus/organics in the soil.
- Low levels of electron acceptors.

A study entitled “Remediation of Chromium(VI) in the Vadose Zone: Stoichiometry and Kinetics of Chromium(VI) Reduction by Sulfur Dioxide,” prepared by Min Ahn and dated August 2003, states, “[the] Cr(VI) can be reduced to Cr(III) by numerous reductants including Fe(II), organic matter and reduced sulfur compounds.” This study shows that the presence of humus or alternate electron acceptors suppresses the conversion of Cr(III) into Cr(VI), as does the presence of reducing conditions.

If a site is documented to have conditions which result in the creation of persistent by-products at detrimental levels, an alternate form of remediation should be considered, or a modification of the ozone injection process should be discussed with the regulator.

Remediation Application

Sometimes dissolved-gasoline concentrations will temporarily increase either in the injection wells or the observation wells as a response to testing. This also indicates some measure of success, as the increase is due to gasoline formerly adsorbed onto soil particles being desorbed through reaction with ozone and transferred to the dissolved state. This is most often observed after installation of an ozone injection system and following several weeks or more of operation. Sustained injection with higher concentrations of ozone should result in declining dissolved gasoline concentrations over time.

For bacterial activity, as mentioned, a one-day test may not create much change. Bacterial growth normally responds best to sustained injection (for example, a series of injection events, or initiation of full-scale remediation). Bacterial colonies usually take between 3 and 6 months to become established after sustained addition of oxygen.

Chapter 18: Remediation
Remediation in the Saturated Zone: In-Situ Groundwater Bioremediation

September 2012

In-situ groundwater bioremediation is a technology that encourages growth and reproduction of indigenous microorganisms to enhance the biodegradation of organic constituents in the saturated zone. *In-situ* groundwater bioremediation can effectively degrade organic constituents which are dissolved in groundwater and adsorbed onto the aquifer matrix.

Advantages of Bioremediation

- Remediates contaminants that are adsorbed onto or trapped within the geologic materials of which the aquifer is composed, along with contaminants dissolved in groundwater.
- Application involves equipment that is widely available and easy to install.
- Creates minimal disruption and/or disturbance to ongoing site activities.
- Time required for subsurface remediation may be shorter than for other approaches.
- Generally recognized as being less costly than other remediation options.
- Can be combined with other technologies (e.g., bioventing, SVE) to enhance site remediation.
- In many cases, this technique does not produce waste products that must be disposed.

Disadvantages of Bioremediation

- Injection wells and/or infiltration galleries may become plugged by microbial growth or mineral precipitation.
- High concentrations (TPH greater than 50,000 ppm) of low-solubility constituents may be toxic to microorganisms and/or not bioavailable.
- Difficult to implement in low-permeability aquifers.
- May require continuous monitoring and maintenance.
- Remediation may only occur in more permeable layers or channels within the aquifer.

Application

In-situ groundwater bioremediation can be effective for the full range of petroleum hydrocarbons. While there are some notable exceptions (e.g., MTBE), short-chain, low-molecular-weight, more water-soluble constituents are degraded more rapidly and to lower residual levels than are long-chain, high-molecular-weight, less-soluble constituents. Recoverable free product should be removed from the subsurface prior to operation of the *in-situ* groundwater bioremediation system. This will mitigate the major source of contaminants as well as reduce the potential for smearing or spreading high concentrations of contaminants.

In-situ bioremediation of groundwater can be combined with other saturated-zone remediation technologies (e.g., air sparging) and vadose-zone remediation operations (e.g., SVE, bioventing).

Operation Principles

Bioremediation generally requires a mechanism for stimulating and maintaining the activity of microorganisms. This mechanism is usually a delivery system for providing one or more of the following: An electron acceptor (oxygen, nitrate); nutrients (nitrogen, phosphorus); and an energy source (carbon). Generally, electron acceptors and nutrients are the two most critical components of any delivery system.

Nutrient injection systems may not be necessary at all if the groundwater contains adequate amounts of nutrients such as nitrogen and phosphorus. Microorganisms require inorganic nutrients such as nitrogen and phosphate to support cell growth and sustain biodegradation processes. Nutrients may be available in sufficient quantities in the aquifer but, more frequently, nutrients need to be added to maintain adequate bacterial populations.

In a typical *in-situ* bioremediation system, groundwater is extracted using one or more wells and, if necessary, treated to remove residual dissolved constituents. The treated groundwater is then mixed with an electron acceptor and nutrients (and other constituents if required), and re-injected upgradient of or within the contaminant source. Infiltration galleries or injection wells may be used to re-inject treated water. Ideally, a "closed-loop" system would be established. This ideal system would continually recirculate the water until cleanup levels had been achieved. An alternative to the "closed-loop" system is to mix the electron acceptor and nutrients with fresh water instead of the extracted groundwater. Extracted water that is not re-injected must be discharged, typically to surface water, sanitary sewer, or to a publicly owned treatment works (POTW).

System Design

In-situ bioremediation can be implemented via a number of treatment modes, including:

- Aerobic (oxygen respiration)
- Anoxic (nitrate respiration)
- Anaerobic (non-oxygen, non-nitrate respiration)
- Co-metabolic

Aerobic treatment has been proven most effective in reducing contaminant levels of aliphatic (e.g., hexane) and aromatic petroleum hydrocarbons (e.g., benzene, naphthalene) typically present in gasoline and diesel fuel. In aerobic treatment, groundwater is oxygenated, some examples include:

- Direct sparging of air or oxygen through an injection well
- Saturation of water with air or oxygen prior to re-injection
- Addition of hydrogen peroxide directly into an injection well or into re-injected water
- Addition of high-oxygen solution

Whichever method of oxygenation is used, it is important to ensure that oxygen is being distributed throughout the area of contamination. Anoxic, anaerobic, and co-metabolic modes are sometimes used for remediation of non-hydrocarbon compounds, such as chlorinated solvents, but are generally slower than aerobic respiration in breaking down petroleum hydrocarbons.

The key parameters that determine the effectiveness of *in-situ* groundwater bioremediation are:

- Hydraulic conductivity of the aquifer, which controls the distribution of electron acceptors and nutrients in the subsurface.
- Biodegradability of the petroleum constituents, which determines both the rate and degree to which constituents will be degraded by microorganisms.
- Location of petroleum contamination in the subsurface.
- Accurate geology through continuous data to develop and maintain an accurate CSM.

For biodegradation to be effective, contaminants must be dissolved in groundwater or adsorbed onto more permeable sediments within the aquifer.

In general, the aquifer medium will determine hydraulic conductivity. Fine-grained media (e.g., clays, silts) have lower intrinsic permeability than coarse-grained media (e.g., sands, gravels). Bioremediation is generally effective in permeable (e.g., sandy, gravelly) aquifer media. However, depending on the extent of contamination, bioremediation can also be effective in less-permeable silty or clayey media. In general, an aquifer medium of lower permeability will require more time to remediate than a more permeable medium.

The location, distribution, and disposition of petroleum contamination in the subsurface can significantly influence the likelihood of success for bioremediation. This technology generally works well for dissolved contaminants and contamination adsorbed onto higher permeability sediments (sands and gravels). However, if the majority of contamination is:

1) in the unsaturated zone,
2) trapped in lower permeability sediments, or
3) outside the “flow path” for nutrients and electron acceptors,

this technology will have reduced or even no impact.

Soil structure and stratification are important to *in-situ* groundwater bioremediation because they affect groundwater flow rates and patterns when water is extracted or injected. Structural characteristics such as micro-fracturing can result in higher permeabilities than expected for certain soils (e.g., clays). In this case, however, flow will increase in the fractured media but not in the unfractured media. The stratification of soils with different permeabilities can dramatically increase the lateral flow of groundwater in the more-permeable strata while reducing the flow through less-permeable strata. This preferential flow behavior can lead to reduced effectiveness and extended remediation times for less-permeable strata.

The biodegradability of a petroleum constituent is a measure of how well it can be metabolized (or co-metabolized) by hydrocarbon-degrading bacteria or other microorganisms. The chemical characteristics of the contaminants will dictate their biodegradability. The biodegradability of organic constituents depends on their chemical structures and physico-chemical properties (e.g., water solubility partition coefficient). Highly soluble organic compounds with low molecular weights will tend to be more rapidly degraded than slightly soluble compounds with high molecular weights. The low water solubilities of the more complex compounds render them less bioavailable to petroleum-degrading organisms. Consequently, the larger, more complex chemical compounds may be slow to degrade or may even be recalcitrant to biological degradation (e.g., asphaltenes in No. 6 fuel oil).

Extreme pH values (i.e., less than 5 or greater than 10) are generally unfavorable for microbial activity. Typically, optimal microbial activity occurs under neutral pH conditions (i.e., in the range of 6 to 8). The optimal pH is site-specific. For example, aggressive microbial activity has been observed at lower pH conditions outside this range (e.g., 4.5 to 5) in natural systems. Because indigenous microorganisms have adapted to the natural conditions where they are found, pH adjustment, even toward neutral, can inhibit microbial activity. If man-made conditions (e.g., releases of petroleum) have altered the pH outside the neutral range, pH adjustment may be needed. If the pH of the groundwater is too low (too acidic), lime or sodium hydroxide can be added to increase the pH. If the pH is too high (too alkaline/caustic), then a suitable acid (e.g., hydrochloric, muriatic) can be added to reduce the pH. Changes to pH should be closely monitored, because rapid changes of more than 1 or 2 units can inhibit microbial activity and may require an extended acclimation period before microbes are able to resume activity.

Extraction wells are generally necessary to achieve hydraulic control over the plume to ensure that it does not spread contaminants into areas where contamination did not previously exist or accelerate the movement toward receptors. Placement of extraction wells is critical, especially in systems that also use nutrient injection wells or infiltration galleries. These additional sources of water can alter the natural groundwater flow patterns, which can cause the contaminant plume to move in an unintended direction or at an unintended rate. Without adequate hydraulic control, this situation can lead to worsening of the original condition and complicate or extend the cleanup.

The goal of the remediation process is to sustain DO levels at 3 ppm, which is the minimum threshold for aerobic degradation.

General Procedures

Pre-test measurements include DO and other monitored parameters, including HPC, as an approximation of expected bacterial activity. These data establish “baseline” or pre-remediation background conditions.

The absence of indigenous bacteria may indicate a lower potential for success in any given environment. In particular, clean sands may be less amenable to aerobic biodegradation due to a lack of substrate for bacteria to colonize.

A general procedure for oxygen uptake studies is as follows:

1) Install a sparging well in the area of proposed treatment.

2) Conduct a routine sparging test to evaluate the ROI. The radius of oxygen diffusion may be slightly higher than the mechanical radius of sparging influence if a diffusion gradient is established between areas of higher and lower relative oxygen content.
3) Inject oxygen into the sparging well until oxygen saturation is attained (i.e., DO levels in excess of 20 ppm). Periodic checks of oxygen levels in the injection well can be made within several hours, days, or weeks of the initial injection.

Data Analysis and Interpretation

The rate of oxygen consumption by the bacteria is calculated on a general basis, depending on how long it takes DO levels to drop either to below 3 ppm or to pre-test levels. The timing of subsequent injections is the frequency required to maintain oxygen in the injection well at the desired steady-state level.

Checking the HPC against pre-test conditions is a *direct indicator* of whether colonies are growing in response to additional oxygen. Declining dissolved-gasoline concentrations are an *indirect indicator* of remediation success.

If dissolved-gasoline concentrations do not show a decline in response to oxygen injection after a few months, either the amount of oxygen is insufficient or biodegradation is not viable for a particular site. Reasons for non-viability can include the hydrocarbon mass being too large or too high in concentration, other background conditions interfering with bacterial growth, or the lack of sufficient substrate for colony growth.

For Example. Peat-bog soils or other natural sources of biological material may preferentially biodegrade in the presence of surplus oxygen. In this case, the oxygen intended to degrade the petroleum contamination is consumed prior to contact with those microorganisms.

Remediation Application

It normally takes six months to a year to fully establish a bacterial colony sufficient to consume significant quantities of hydrocarbon mass. Wells are spaced in accordance with the calculated ROI to provide full plume coverage, or are spaced in a barrier arrangement to prevent/limit off-site downgradient migration.

Sometimes a temporary increase in dissolved gasoline concentrations may be observed as the bacterial colonies become established: biosurfactants generated as a by-product of bacterial activity cause the desorption of adsorbed constituents from saturated-zone soil particles. This is most common at sites where the majority of the soil plume mass is below the water table. With sustained conditions hospitable to colony growth, the temporary increase in dissolved gasoline usually dissipates quickly. The installation of downgradient sentry monitoring wells to watch for plume detachment may be necessary in some cases.

Chapter 18: Remediation
Remediation in the Saturated Zone: Groundwater Extraction

September 2012

Groundwater Extraction

Groundwater extraction is a common method for treating contaminated groundwater at LUFT sites. The two most common groundwater extraction processes are:

- Pump-and-treat technology utilizes a submersible pump installed in a groundwater extraction well. The pump withdraws water to the surface to be treated before discharge.
- Dual-phase extraction technology combines SVE with pump-and-treat technology.

These technologies are described in greater detail below.

History. Groundwater extraction is a remediation process which has been used for over 20 years in the LUFT industry.

Pump-and-Treat

In a pump-and-treat system, contaminated groundwater or mobile NAPLs are captured in the saturated zone and pumped to the surface for treatment (EPA 1990). Pump-and-treat systems are used primarily to accomplish the following:

- **Hydraulic containment**. To control the movement of contaminated groundwater, preventing the continued expansion of the contaminated zone.
- **Treatment**. To reduce the dissolved contaminant concentrations in groundwater sufficiently that the aquifer complies with cleanup standards, or the treated water withdrawn from the aquifer can be put to beneficial use (EPA 1995).

Advantages

- Proven performance, readily available equipment; easy installation.
- Minimal disturbance to site operations; can be used under buildings without excavation.
- Can be applied at sites with free product, and can be combined with other technologies.
- Can be used in unconfined aquifers.
- Resource can be treated and re-used.

Disadvantages

- May require long operation time to achieve desired results.
- May not be effective in low-permeability soils.
- Large volume of extracted groundwater may require treatment.
- Requires complex monitoring and control during operation.

Application

In order for pump-and-treat to be an effective remedial solution, the physicochemical subsurface must allow contaminants to flow to the extraction wells. Consequently, the subsurface must have sufficient hydraulic conductivity (K) to allow fluid to flow readily and the chemicals must be transportable by the fluid (EPA 1990).

Cases in which contaminants cannot readily flow to pumping wells include:

- Heterogeneous aquifer conditions where low-permeability zones restrict contaminant flow toward extraction wells.
- Chemicals that are adsorbed or precipitated to the soil and slowly desorb or dissolve back into the groundwater as chemical equilibrium changes in response to the extraction process.
- Immobile NAPLs that may contribute to a miscible contaminant plume by prolonged dissolution (i.e., a separate-phase gasoline at residual saturation, EPA 1990).

In these cases, modifications to pump-and-treat technology, such as pulsed pumping, may be appropriate. Pump-and-treat may also be used in combination with other remedial alternatives, such as SVE and/or bioremediation.

The main limitation of pump-and-treat remediation is the long period of time that may be required to achieve an acceptable level of cleanup. The other issue with pump-and-treat technology at LUFT sites is that oily hydrocarbons can become trapped in the pore spaces by capillary forces and cannot readily be pumped out (EPA 1990).

Technologies which feature methods to address soils below the water table in combination with pump-and-treat systems can be more successful. Because oxygenates tend to have lower rates of adsorption, groundwater plumes composed primarily of oxygenates may respond well to simple groundwater extraction as a remediation process.

Further details regarding system design and operation and maintenance of pump-and-treat systems are available in EPA's 1990 publication, *Basics of Pump-and-Treat Ground-Water Remediation Technology* (EPA 1990).

Dual-Phase Extraction

Dual-phase extraction (DPE), also known as multi-phase extraction, vacuum-enhanced extraction, or sometimes "bioslurping," is an *in-situ* technology that uses pumps to remove various combinations of contaminated groundwater, separate-phase petroleum product, and hydrocarbon vapor from the subsurface. Extracted liquids and vapor are treated and collected for disposal, or re-injected to the subsurface, where applicable (EPA 1994).

Advantages

- Proven performance over a wide range of conditions. Requires no downhole pumps, but is flexible enough to allow their use if necessary.
- Minimal disturbance to site operations; can be used under buildings without excavation.
- Short treatment times (usually 6 months to 2 years under optimal conditions).
- Substantially increases groundwater extraction rates.
- Can be applied at sites with free product, and can be combined with other technologies.
- Can reduce the cost of groundwater treatment through air stripping within the vacuum-extraction tube.

Disadvantages

- Single-pump systems are expensive to implement at sites with medium- to high-permeability soils; dual-pump systems may not be effective in low-permeability soils.
- Difficult to apply to sites where the water table fluctuates, unless water-table depression pumps are employed.
- Treatment may be expensive for extracted vapors and for oil-water separation.
- Large volume of extracted groundwater may require treatment.
- Requires specialized equipment with sophisticated control capability.
- Requires complex monitoring and control during operation.

Application

DPE systems can be effective in removing separate-phase product (free product) from the subsurface, thereby reducing concentrations of petroleum hydrocarbons in both the saturated and unsaturated zones of the subsurface. DPE systems are typically designed to maximize extraction rates; however, the technology also stimulates biodegradation of petroleum constituents in the unsaturated zone by increasing the supply of oxygen.

DPE is often selected because it enhances groundwater and/or product recovery rates, especially in layered, fine-grained soils. The application of DPE also maximizes the effectiveness of SVE by lowering the water table and thereby increasing air-phase permeabilities in the vadose zone (EPA 1994).

Operating Principles

The vacuum applied to the subsurface with DPE systems creates vapor-phase pressure gradients toward the vacuum well. These vapor-phase pressure gradients are also transmitted directly to the subsurface liquids present, and those liquids existing in a continuous phase will flow toward the vacuum well in response to the imposed gradients. The higher the applied vacuum, the larger the hydraulic gradients that can be achieved in both vapor and liquid phases, and thus the greater the vapor- and liquid-recovery rates.

Dramatic enhancements in both water- and petroleum-product recovery rates resulting from the large hydraulic gradients attainable with DPE systems are possible. The depressed groundwater table that results from these high recovery rates serves both to hydraulically control groundwater migration and to increase the efficiency of vapor extraction. The remedial effectiveness of DPE within the zone of dewatering that commonly develops during DPE application should be greater than that of air sparging due to the more uniform air flow developed using DPE (EPA 1994).

Further details regarding system design and operation and maintenance of dual-phase extraction systems are available in EPA's 1994 publication, *How to Evaluate Alternative Cleanup Technologies for Underground Storage Tank Sites: A Guide for Corrective Action Plan Reviewers* (EPA 1994).

Chapter 18: Remediation

Remediation in the Saturated Zone: Natural Attenuation

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The ASTM International, formerly known as American Society for Testing and Materials (ASTM) defines natural attenuation as "a potential remediation alternative for containment and reduction of the mass and concentration of petroleum hydrocarbons in the environment to protect human health and the environment. Remediation by natural attenuation depends upon natural processes such as biodegradation, dispersion, dilution, volatilization, hydrolysis, and sorption to attenuate petroleum constituents of concern to achieve remedial goals" (ASTM, E1943-98). Another important element of natural attenuation is that it occurs without human intervention.

Remediation by natural attenuation is usually used in conjunction with other remedial technologies or as a follow-up to active remediation to answer questions such as: 1) Is the plume stable? 2) Are concentrations of COCs decreasing? 3) What are the degradation rates? These questions are asked to determine whether natural attenuation will degrade COCs prior to the groundwater being used as a future beneficial resource.

Natural attenuation processes include a variety of physical, chemical, and biological processes that, under favorable conditions, reduce the mass, toxicity, mobility, volume, and/or concentration of contaminants in soil and/or groundwater. Processes that result only in reducing the concentration of a contaminant are termed "non-destructive" and include hydrodynamic dispersion, sorption, and volatilization. Other processes, such as biodegradation and abiotic degradation (e.g., hydrolysis), result in an actual reduction in the mass of contaminants and are termed "destructive" (EPA 1994). For petroleum hydrocarbons, biodegradation is the most important (and preferred) attenuation mechanism, since it is the only natural process that results in an actual reduction in the mass of petroleum hydrocarbons.

Advantages of Natural Attenuation

In contrast to conventional engineered remediation technologies, natural attenuation offers a number of advantages, especially if intrinsic bioremediation is occurring:

- During intrinsic bioremediation, contaminants can ultimately be transformed to innocuous by-products (e.g., carbon dioxide and water in the case of fuel hydrocarbons), not just transferred to another phase or location within the environment.
- Natural attenuation is non-intrusive and allows continuing use of infrastructure during remediation.
- Natural attenuation does not involve generation or transfer of wastes.
- Natural attenuation is often less costly than other currently available remediation technologies.
- Natural attenuation can be used in conjunction with, or as a follow-up to, "intrusive" remediation measures.
- Natural attenuation is not subject to limitations imposed by the use of mechanized remediation equipment (e.g., no equipment downtime).

Disadvantages of Natural Attenuation

Natural attenuation has the following potential disadvantages:

- Time frames for complete remediation may be long.
- Responsibility must be assumed for associated monitoring and its associated cost, and the implementation of institutional controls.
- Natural attenuation is subject to natural and anthropogenic changes in local hydrogeologic conditions, including changes in groundwater flow direction or velocity, electron acceptor and donor concentrations, and potential future releases.

- The hydrologic and geochemical conditions amenable to natural attenuation are likely to change over time and could result in renewed mobility of previously stabilized contaminants and may adversely impact remediation effectiveness.
- Aquifer heterogeneity may complicate site characterization, as it will with any remediation approach.

Indicators and Parameters

Multiple distinct, but converging, lines of evidence are used to evaluate natural attenuation. The most common lines of evidence used to demonstrate natural attenuation of organic compounds dissolved in groundwater are historical trends, geochemical data, and microbiological data (as pioneered by the Air Force Center for Engineering and the Environment [AFCEE] in the 1990s).

Secondary parameters that are indicative of natural attenuation include, but are not limited to, pH, DO, ORP, sulfate, nitrate, Fe(II)/Fe(III) ratios, methane, and MTBE/TBA ratios. Additionally, aerobic bacterial population analysis (HPC) can be a useful indicator of indigenous microbial activity.

- **Historical trends**. The first line of evidence for natural attenuation is historical data that demonstrate a clear and meaningful trend of decreasing concentrations over time at appropriate monitoring points, which suggest a plume that is stable or retreating. A stable or retreating plume indicates that biodegradation is removing the mass of dissolved contaminants from the groundwater at a rate equal to or greater than the source is adding them to the plume. An increase in daughter-compound concentrations can also indicate biodegradation of the original compound: for example, decreases in the MTBE/TBA ratio as MTBE degrades to TBA.
- **Geochemical data**. A second line of evidence for natural attenuation involves geochemical indicators. Groundwater chemistry analytical data showing that geochemical conditions are suitable for biodegradation and that active biodegradation has occurred are indicated by: 1) Consumption/depletion of electron acceptors and donors, i.e., oxygen, nitrate, and sulfate, or 2) Production/increase of metabolic by-product concentrations, i.e., dissolved iron (II), manganese (II), and methane.

Drilling Down. Lower levels of oxygen, nitrate, and sulfate within a groundwater plume compared to upgradient or downgradient areas indicate that these parameters have decreased within the plume; they may be evidence of biodegradation. Conversely, higher levels of methane, Fe(II), and manganese II within a plume compared to non-plume areas indicate that biodegradation is occurring within the plume area.

- **Dissolved oxygen (DO)**. DO concentrations less than about 0.5 mg/L generally indicate that an anaerobic pathway exists. Field measurements made with electrodes are typically preferred over laboratory data. Samples should be protected from exposure to oxygen during sampling and analysis, as field measurement data reliability is a concern.
- **Microbiological data**. A third line of evidence for natural attenuation involves microbiological laboratory data (e.g., HPCs) or field data, which can be used to show that indigenous biota are capable of degrading site contaminants.

Typically, the use of electron acceptors is energetically favorable, meaning organisms which can use this compound for respiration will degrade waste compounds the most rapidly. The inventory below lists compounds in order of energetic favorability.

1) Aerobic respiration (oxygen use)
2) Denitrification (nitrate used as substrate)
3) Manganese (IV) reduction
4) Ferric iron (Fe[III]) reduction
5) Sulfate reduction
6) Methanogenesis

Table 18-5 describes various analytes likely to be present in samples collected at LUFT sites and the trends in analyte concentrations that will be visible if biodegradation is occurring.

Table 18-5: Trends in Contaminant, Electron Acceptor, and Metabolic By-Product Concentrations during Biodegradation

Analyte	Trend in Analyte Concentration During Biodegradation	Terminal Electron Accepting Processes Causing Trend
Petroleum Hydrocarbons	Decreases	Aerobic Respiration, Denitrification, Manganese (IV) Reduction, Fe(III) Reduction, Sulfate Reduction, Methanogenesis
Dissolved Oxygen (DO)	Decreases	Aerobic Respiration
Nitrate	Decreases	Denitrification
Manganese (II)	Increases	Manganese (IV) Reduction
Fe(II)	Increases	Fe(III) Reduction
Sulfate	Decreases	Sulfate Reduction
Methane	Increases	Methanogenesis
Chloride	Increases	Reductive Dechlorination or Direct Oxidation of Chlorinated Compound
Oxidation-Reduction Potential (ORP)	Decreases	Aerobic Respiration, Denitrification, Reduction, Fe(III) Reduction, Sulfate Reduction, Methanogenesis, and Halorespiration
Alkalinity	Increases	Aerobic Respiration, Denitrification, Fe(III) Reduction, and Sulfate Reduction

Data Collection

The indicators and parameters of natural attenuation are monitored for a period of time and the duration of monitoring is specific to each LUFT site. Historically, there has been a belief that natural attenuation requires a long-term monitoring program. Current practical data suggest that, if trends are shown consistently over the course of a year accounting for fluctuations in groundwater elevations, long-term monitoring is not necessary.

Data collection for natural attenuation may not be needed at all of the monitoring well locations at a LUFT site. With the approval of the agency case worker, the select wells and/or specific frequencies can be determined such that the level of data collected is accurate to demonstrate the decreasing trends of COCs, plume stability, etc. Most importantly, monitoring should be conducted only until it has been demonstrated that natural attenuation will continue and eventually meet remedial goals, prior to the resource being needed for a beneficial use, and not for extended periods of time beyond what is needed to establish a data trend.

Further Reading.

This text is an excerpt from the following website:

http://www.afcee.af.mil/resources/technologytransfer/programsandinitiatives/monitorednaturalattenuation/long-termmonitoring/index.asp

Chapter 18: Remediation
Remedial Effectiveness

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After a remedial technology is installed and operational, it is important to determine whether that technology is effective. Generally, declining trends in extracted vapor and/or groundwater are evidence of success.

Declining groundwater concentrations of COCs as compared with data collected before the onset of remediation are evidence of success. Evidence of **in**effectiveness includes groundwater concentrations of COCs that persist at or near levels observed before the start of cleanup. Increases in concentrations in wells downgradient from the treatment area may indicate a detrimental effect; for example, incomplete oxidation during ozone sparging. In such cases, the process is promptly stopped to examine potential problems and plan further action.

Exceptions to this generalization include temporary increases in groundwater concentrations in the treatment area shortly after initiation of some forms of remediation. These can be a sign of successful implementation. For example, increases in dissolved-gasoline concentrations after initiation of air sparging in the source area usually represent COCs being stripped from soils below the water table by the sparging process, followed by dissolution in the groundwater. Continued sparging should result in decreasing concentrations over time following the initial "spike" in levels. This effect is also seen during enhanced bioremediation, due to surfactants produced by the microbes as a by-product of metabolism.

For many of these assessments, readily available geographical information systems (GIS) software and simple trend-analysis statistical tools are very useful for data visualization and performance assessment; such tools can enhance data-analysis capabilities.

Further Reading.

Information from this chapter and further information are available from "Evaluating Remedy Performance" (from *Remediation Process Optimization: Identifying Opportunities for Enhanced and More Efficient Site Remediation*, 2004, prepared by The Interstate Technology & Regulatory Council [ITRC] Remediation Process Optimization Team).

One of the challenges of effective remediation is determining when remediation is complete. If the RP, in partnership with his/her consultant, does not efficiently manage the endpoint of the remediation process, the lack of operational limits (shutdown criteria) can result in significant, unnecessary costs to both the RP and the UST Cleanup Fund.

In general, once extracted media (vapors, groundwater) or dissolved-plume concentrations decline to stable minimum levels (the third, diffusional stage of extraction), the effective performance limit of the remediation process has been reached. Once it is clear that the remediation system has reached this performance limit, the site's path forward is revisited with the lead agency.

If the remediation system performance limit is reached and concentrations remain above remediation goals after verification testing, potential options to be discussed with the regulatory case worker may include

- Installation of a new remediation system with different performance goals,
- Risk modeling of remaining concentrations in lieu of further physical treatment, and/or
- Deed restrictions, if approved by the property owner.

If reaching equipment performance limits, however, coincides with concentration declines in soil and/or groundwater to defined goals, then remediation is by definition fully complete.

Chapter 18: Remediation
Lessons Learned

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Introduction

This section contains "lessons learned" for designing and implementing a successful remedial action. These tips may not be valid for all types of remediation and are dependent on site conditions. It is recommended that the RP and/or consultant contact the lead regulatory agency for ideas and suggestions on how to execute a remedial action.

Explore Funding Sources

The contamination at many sites is left un-remediated and may pose a risk to human health and the environment, due to the inability of RPs to fulfill the financial responsibility requirements for investigation and/or cleanup or, in some cases, a site has been abandoned. RPs may apply for funding opportunities through the California Underground Storage Tank Cleanup Fund. The UST Cleanup Fund chapter describes this process in greater detail. The RP and/or lead regulatory agency may also explore and apply for funding through the Emergency, Abatement, and Recalcitrant (EAR) Program, the Orphan Site Cleanup Fund Program, the Contamination Orphan Site Cleanup Subaccount Program, and the School District Account (Assembly Bill 2729). Please see the follow website for more information on these funding resources: http://www.swrcb.ca.gov/water_issues/programs/ustcf/

Immediate Source Area Removal

It is recommended to make every effort to conduct remedial activities (including over-excavation of soil) in the source area immediately after tank removal and not to postpone them until a full investigation, which can take years, is complete. It can be much cheaper, easier, and quicker to remediate the contamination immediately.

Plan According to Site–Specific Conditions

Understanding specific site conditions is imperative for the successful design and implementation of a remedial action. The following includes tips and methods for planning different types of site-specific conditions.

Continual Strategic Planning

When writing the first assessment work plan, it is recommended that the project manager assemble the geologists and remediation engineers to establish the list of data needs that can be collected with the first and each subsequent field assessment. For example, depending upon the soils encountered, various remediation technologies may be of limited use later in a project. Knowing this early in the project, the remediation engineers can steer the extra sampling needs toward technologies that may work with the site specific conditions present. After the data has been received from each assessment event, the team can re-assemble to reestablish future needs. This practice will maximize the budget of a project and effectiveness of a remediation.

During the feasibility study stage of the project, consider the entire problem and all potentially affected media; soil, groundwater, and soil vapor, and address them all when the first remediation system is installed. A "completed at the beginning of the project" approach can be the easiest way of ensuring that all elements of a site are included. See the Conceptual Site Model chapter for more information.

Important! Know the end point (i.e., what are all the closure requirements and remediation goals?) when starting to design a remediation system. Then plan the design with a remediation technology or a series of remediation technologies that will efficiently reach those goals.

Avoid Risk of Contaminant Migration

Extraction wells and injection wells can be direct conduits to other aquifers and, if not sealed, can cause contamination to migrate from one aquifer to another. When designing a remediation system, always keep site-specific geology and hydrogeology in mind, including the location and depths of all aquifers when drilling.

Remedial Design Based on Site Conditions

UST are located almost everywhere, from remote locations that are only seasonably accessible to industrial properties to neighborhoods. Understanding the site-specific location characteristics is essential to implementing a successful site remediation. Issues to consider when implementing a remedial design in different types of locations include:

Light Pollution. Security lighting at a site may negatively impact the neighborhood. A possible solution to minimize light pollution is to use motion sensors or subdued lighting within the treatment compound.

Noise Pollution. Specifically for air-sparging and vapor-extraction systems, the compressors and blowers produce a lot of air and, if exhausted through too small a discharge pipe, will produce a very annoying whistle or whining noise. Noise issues may disrupt neighbors. Several solutions include constructing a well-insulated structure to house the equipment, using noise blankets, and muffling or redirecting the discharge piping.

Discharge of Treated Groundwater via Infiltration Gallery. Knowing the local geology and infiltration rates is essential. There can be problems if water is discharged on the site and it daylights a few hundred feet away on an adjacent property.

Energy Source. Examine the availability of power – will a new electrical drop be needed, what voltage is available, will natural gas be needed, and what is the lead time for the utility? Before ordering equipment, contact the power company and request a written statement as to the voltage service with which the three-phase voltage systems will be connected to the system. If a three-phase, 230-volt service is assumed, and the equipment is ordered and installed to a three-phase, 208-volt service, the system will not work as designed and the equipment service life will be severely limited.

Understand the reliability of the power service in the vicinity and make preparations for re-start, where necessary. Power disruptions stop remediation, for example, in erratic winter weather. When a site is located in remote or rural areas and where weather can disrupt power for short time periods, the system may be off until a technician can return to restart the system, and weeks of remediation could be lost. In remote locations, such as in the Sierra Nevada, where self-generated power locations with routine maintenance on generators can cause disruptions in power, automatic restart functions can be designed to restart the system once power is restored.

Access Issues. Remote locations, for example, a cell tower near the crest of the Sierra Nevada, may be accessible for only 8 months per year to vehicular traffic. Other means of access will have to be considered in the operations and maintenance costs. Additionally, some LUFT sites are very small and may not be able to accommodate a large remediation system or the heavy machinery needed to install it.

Weather Conditions. With the decentralized operation of some firms, sometimes a remedial designer may be from another part of the country and may design the system based on knowledge of his or her own locale, and sometimes not be aware of site-specific conditions, including weather conditions. When designing a remediation system, the local weather conditions should be considered; for example, to winterize all exposed water piping, covering containment berms to avoid flooding equipment, or providing a new home or curiosity for unwanted fauna (bats, wasps, snakes, scorpions, rodents, bears, etc.)

Permitting and Approvals. Determine all the permitting and approvals that may be needed to install and implement a remedial design. If water will be discharged, will the sanitation district need to approve the permit, or will a general waste discharge permit be required, and how long with this procedure take? Additionally, determine whether there are other agencies that may have input to the remedial design. Is there an architectural or planning committee that must approve your design to ensure that the housing or enclosure of the remedial system meets the architectural standards of the area?

See the Health and Safety chapter for requirements and other issues that need to be considered and budgeted for working in the field.

Analysis of a Remediation System

Performance Criteria and Effectiveness

Prior to installation of a remediation system, estimate the performance criteria and cleanup schedule, so that when operational, the system can be evaluated (e.g., gallons of groundwater treated per day or pounds of petroleum vapor recovered per unit of time). This can be used to establish when the system will no longer be effective; for example, when influent concentrations have reached a point where the remediation technology is not cost-effective.

Sampling for Remediation Technology Selection and Potential Issues

During the first round of assessment at a site, consider collecting additional, non-required data. Continuously core a minimum of two borings and log very carefully. This will provide information on whether the site has small seams of more permeable materials in the soil matrix or distinct zones of more permeable material, which will assist in designing the remedial system. Collect several core samples from distinct soil horizons and analyze for geotechnical properties, such as soil moisture, density, grain size, porosity, metal content, etc. Additionally, collect a minimum of one groundwater sample for water quality analysis (metals, hardness, alkalinity) and biological testing such as *E. coli* and *coliform* (if septic tanks are in the area). These tests will assist in the remediation technology selection and potential operation and maintenance issues later in the project.

Note. Revisiting and revising the CSM as new data become available is an effective way to continually analyze site conditions and remedial actions implemented. Communication and collaboration between the RP, consultant, and lead regulatory agency(ies) regarding the site status is imperative to maintain efficient and cost-effective remediation.

Chapter 18: Remediation
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Section 4: Glossary and Acronyms

Chapter 19: Glossary

September 2012

Scope of This Chapter

This Glossary provides the definitions of terms used in this Manual.

Many terms in this Glossary are ordinary words used in daily life (“gasoline”); others are “terms of art” (i.e., specific to this kind of work) and may be used differently in LUFT contexts as opposed to other contexts. If there is any doubt about the meaning of a term found in the CA LUFT Manual, please look for it here. If the term in question isn’t in the Glossary, it’s most likely

- a professionally defined, specific, non-ambiguous term (e.g., well boring logs, Unified Soil Classification System) or
- a chemical compound or group of compounds whose specific structure or behavior is best illustrated, described, and/or modeled on the Internet or in a chemistry textbook

Any terms which refer to trademarked or registered product names are understood to include the ™ or ® mark throughout this California LUFT Manual, even if not printed at each mention of the product name.

Entries in this Glossary are presented in alphabetical order and have been **shown in this font** whenever they appear under the definition of another term. **Boldface** and *italics* have been used here for their normal purposes. When an entry in this Glossary is also known by another name, that secondary name is shown in SMALL CAPITAL LETTERS under the primary definition (for an example, see **Cyclic alkanes**).

Abandoned well

- A groundwater well used less than 8 hours in any 12-month period.
- A monitoring well is considered “abandoned” or permanently inactive if it has not been used for one year, unless the owner demonstrates intention to use the well again (DWR 2002). A well which is in such a state of disrepair that it cannot be made functional for its original use or for any other use regulated by this Manual.
- An engineering test hole after 24 hours or more have elapsed since the construction and testing work at the site were completed.

From http://wwwdpla.water.ca.gov/sd/groundwater/california_well_standards/mws/mws_section16-18.html and http://search.municode.com/html/16749/level3/D4_C8_A1.html#D4_C8_A1_4812

Advection

Advection is the transport of dissolved constituents with groundwater and is, therefore, dependent on the **hydraulic conductivity** of the subsurface materials and hydraulic gradient in the aquifer. From the Fate and Transport chapter.

Aerobic biodegradation

The breakdown of organic contaminants by micro-organisms when oxygen is present. Aerobic bacteria use oxygen as an electron acceptor, and break down organic chemicals into smaller organic compounds, often producing carbon dioxide and water as the final products. Aerobic biodegradation is also known as AEROBIC RESPIRATION. Aerobic biodegradation is an important component of the natural attenuation of contaminants at many hazardous-waste sites.

From http://toxics.usgs.gov/definitions/aerobic_biodegradation.html

Air toxics

Chemicals released into the air that are known or suspected to cause cancer, or other serious health problems, such as birth defects or reproductive effects. Vehicle exhaust contains substantial amounts of air toxics. The

California Air Resources Board (CARB) has identified diesel exhaust particulate as the #1 air-borne carcinogen in the state.
From http://www.sbcapcd.org/sbc/pollut.htm (Santa Barbara County Air Pollution Control District)

Alcohols

Any of a series of *hydroxyl compounds*, the simplest of which are derived from saturated hydrocarbons and have the general formula $C_nH_{2n+1}OH$, including methanol (CH_3OH) and ethanol (C_2H_5OH). (*Hydroxyl compounds* contain an oxygen atom and a hydrogen atom bonded covalently to one another.)

Aliphatic compounds

Of, relating to, or designating a group of organic chemical compounds in which the carbon atoms are linked in open chains or in ring compounds without double bonds (***vs.* aromatics**, where the carbon atoms are arranged in ring structures that have double bonds in them). The carbon atoms can be joined by single, double, or triple bonds. Examples of aliphatic compounds are shown in the chapter on Fate and Transport.

Alkanes

Alkanes are chemical compounds consisting only of the elements carbon (C) and hydrogen (H) (i.e., hydrocarbons), in which these atoms are linked together exclusively by single bonds (i.e., they are saturated compounds) without any cyclic structure or "loops." The alkanes form a group of saturated, open-chain hydrocarbons having the general formula C_nH_{2n+2}—for example, CH_4, C_2H_6, C_3H_8, etc.

Alkenes

Alkenes are unsaturated chemical compounds containing at least one C-C double bond. The simplest non-cyclic alkenes, with only one double bond and no other functional groups, form a homologous series of hydrocarbons with the general formula C_nH_{2n} (for example, ethylene gas, C_2H_4).

Alkyl groups

Alkyl groups are hydrocarbons (C + H); typically an alkyl group is a part of a larger molecule. The term is usually used loosely; there is no general formula for an alkyl group. In structural formulae, an alkyl group is represented with an "R." Usually, alkyl groups resemble hydrocarbons, but with one less hydrogen atom. The smallest alkyl group is a methyl (CH_3).

Anaerobic biodegradation

The breakdown of organic contaminants by micro-organisms when oxygen is not present. Some anaerobic bacteria use nitrate, sulfate, iron, manganese, or carbon dioxide as their electron acceptors, and break down organic chemicals into smaller compounds, often producing carbon dioxide and methane as the final products. This general mechanism of anaerobic biodegradation is an example of *anaerobic respiration*. Alternatively, some anaerobic microorganisms can break down organic contaminants by *fermentation*. *Fermentation* takes place when the organic chemical acts as an electron acceptor. Anaerobic biodegradation is an important component of the natural attenuation of contaminants at many hazardous-waste sites.

From http://toxics.usgs.gov/definitions/anaerobic_biodegradation.html

Analyte(s)

Compound(s) for which an analytical laboratory has been requested to analyze a given sample or set of samples.

Anoxic

*A*n adjective that means "without oxygen." For example, anoxic groundwater contains no dissolved oxygen. Anoxic groundwater conditions at hazardous-waste sites are common because **biodegradation** processes often use up all the available oxygen. A related term is **anaerobic**.

From http://toxics.usgs.gov/definitions/anoxic.html

Anthropogenic

Caused by human beings as opposed to the processes of nature.

Aquiclude

A body of rock that will absorb water slowly but will not transmit it fast enough to supply a well or spring.
From *Dictionary of Geological Terms*.

Aquifer

An aquifer is an underground layer of water-bearing permeable rock or unconsolidated materials (gravel, sand, silt, or clay) from which groundwater can be usefully extracted using a water well. An aquifer provides groundwater for drinking, irrigation, and other beneficial uses. In California, the protection of groundwater quality in aquifers (and other bodies of fresh water) is within the purview of the State Water Resources Control Board (State Water Board).

Aquitard

A body of impermeable or distinctly less permeable material stratigraphically adjacent to one or more **aquifers** which retards but does not prevent the flow of water to or from an adjacent **aquifer**. An aquitard does not readily yield water to wells or springs, but may serve as a storage unit for groundwater.

Aromatic compounds

Hydrocarbons, compounds composed of carbon and hydrogen, are divided into two classes: aromatic compounds, which contain one or more aromatic rings (i.e. a ring with double bonds, such as benzene), and **aliphatic compounds**, which do not contain aromatic rings (see the Fate and Transport chapter).

Benzene, toluene, ethylbenzene, and xylenes (BTEX)

Benzene, toluene, ethylbenzene, and xylenes ("BTEX") are four **volatile organic compounds (VOCs)** found in gasoline. They are mobile in the subsurface and in the atmosphere, and of concern for underground storage tank (UST) remediation sites due to their mobility and toxicity. Because they are found together and are similar in their chemical properties, they're often referred to by the acronym BTEX (BEE-TEX).

Best Management Practices (BMPs)

Practical and effective measures to protect natural resources. Historically, the term has referred to pollution controls in the fields of industrial wastewater control and municipal sewage control, while in stormwater management (both urban and rural) and wetland management, BMPs may refer to a principal control or treatment technique as well.

Biodegradation

Biodegradation is the breakdown of organic contaminants into smaller compounds by microbial organisms. The microbial organisms transform the contaminants through metabolic or enzymatic processes. Biodegradation processes vary greatly, but frequently the final product of the degradation is carbon dioxide or methane. Biodegradation is a key process in the natural attenuation of contaminants at LUFT sites.

From http://toxics.usgs.gov/definitions/biodegradation.html

Capillary fringe

The capillary fringe is the mostly saturated (or completely saturated) zone just above the water table in which groundwater is drawn up from a water table by capillary action. Water content decreases with distance above the water table. Pores at the base of the capillary fringe are fully saturated due to tension saturation. If pore size is small and relatively uniform, it is possible that soils can be completely saturated with water for several feet above the water table. Alternately, the saturated portion will extend only a few inches above the water table when pore size is large.
See the Fate and Transport chapter for an illustration.

centiPoise (cP)

The unit used to express dynamic viscosity. Water at 20 °C has a viscosity of 1.0020 cP, or 0.001002 kilogram/meter second.

$$1\ \mathrm{P} = 1\ \mathrm{g{\cdot}cm^{-1}{\cdot}s^{-1}}$$

More at http://en.wikipedia.org/wiki/Viscosity

Co-metabolic, co-metabolism

When two or more **micro-organisms** are required for the **biodegradation** of petroleum hydrocarbons, they are said to be co-metabolizing the target hydrocarbon(s). Some compounds that are resistant to standard monocultural **biodegradation** (by a given species of bacterium, for example) have proved to be biodegradable with combinations of two, three, or more different species.

Confined aquifer

An **aquifer** separated from the ground surface or from an overlying aquifer by an **aquiclude** or an **aquitard** (usually a layer of non-porous clay-type soil) to the extent that pressure can be created in the lower reaches of the **aquifer** without affecting either the soil surface or the upper reservoir of water.

Consultant

The consultant is defined as a third party (not the **responsible party [RP]** and not a regulator), generally a licensed and experienced professional geologist or environmental engineer, hired by an **RP** to perform tasks associated with the investigation and remediation of a LUFT site.

Constituent(s) of concern (COCs)

Contaminants in environmental media that may cause a risk to human health, safety, or the environment that have been identified for further evaluation, such as a risk assessment.

Cyclic alkanes

Cycloalkanes (also called NAPHTHENES, especially if from petroleum sources) have one or more rings of carbon atoms in their chemical structure. Like **alkanes**, cycloalkanes consist of only carbon (C) and hydrogen (H) atoms and are saturated; there are no double or triple C-C bonds. The general chemical formula for cycloalkanes is $C_nH_{2(n+1-g)}$, where g = the number of rings in the molecule. A cycloalkane with a single ring is named in parallel with its non-cyclic **alkane** counterpart possessing the same number of carbon atoms: cyclopropane (C_3H_6) ***vs.*** propane (C_3H_8), cyclobutane (C_4H_8) ***vs.*** butane (C_4H_{10}), etc.

Data Quality Objectives (DQOs)

DQOs are qualitative and quantitative statements specified to ensure that data of known and appropriate quality are obtained. The DQO process is a series of planning steps, typically conducted during site assessment and investigation, that is designed to ensure that the type, quantity, and quality of environmental data used in decision making are appropriate. The DQO process involves a logical, step-by-step procedure for determining which of the complex issues affecting a site are the most relevant to planning a site investigation before any data are collected.

From http://www.brownfieldstsc.org/glossary.cfm?lett=D

Destroy

To fill a well completely, usually with concrete (including both interior and annular spaces, if the well is cased), so that it will not produce water or act as a conduit for the transmission of water between any water-bearing formations penetrated.

Detection Limits

DETECTION LIMIT – the lowest amount that can be distinguished from the normal “noise” of an analytical instrument or methods.

INSTRUMENT DETECTION LIMIT – the lowest amount of a substance that can be detected by an instrument without correction for the effects of sample matrix, handling, and preparation.

METHOD DETECTION LIMIT – the detection limit that takes into account the reagents, sample matrix, and preparation steps applied to a sample in specific analytical methods.

SAMPLE QUANTITATION LIMIT – a quantitation limit that accounts for sample characteristics, sample preparation, and analytical adjustments, such as dilution.

The above four terms from: http://www.deq.virginia.gov/Programs/LandProtectionRevitalization/RemediationProgram/VoluntaryRemediationProgram/VRPRiskAssessmentGuidance/Glossary.aspx

REPORTING LIMIT – The lowest concentration at which a contaminant is reported.

Diesel, "middle-weight" hydrocarbons

Diesel fuel #2 (also fuel oil #2) is composed primarily of C10 to C25 hydrocarbons, including **aliphatics**, minor amounts of monoaromatics, and **Polycyclic Aromatic Hydrocarbons (PAHs)** (EPA 1996). Diesel fuel and fuel oils are much less chemically complex than **gasoline**, and their components have not changed very much throughout manufactured history. Besides diesel, other middle-distillate fuels include:

- Kerosene (approximately C8 to C18),
- Kerosene-based jet fuels [e.g., Jet A or JP-5 (C8 to C18) or JP-8 (C8 to C20)],
- Diesel fuel #1 or fuel oil #1 (approximately C8 to C22), and
- Heavier fuel oils such as marine diesel or diesel / fuel oil #4 (approximately C12 to C30).

See the Fate and Transport chapter.

Dipping strata

Non-horizontal sediments or layers of bedrock / formation whose inclination from the horizontal affects the migration of subsurface substances.

Dispersion

Dispersion is the spread of dissolved constituents predominantly in the direction of groundwater flow, but also in directions other than would be expected due to groundwater movement only (lateral and vertical). Dispersion causes some attenuation of the concentrations (lower concentrations) as the constituent moves downgradient.

From the Fate and Transport chapter.

Effective Solubility

The maximum dissolved-phase concentration when a compound is part of a chemical mixture. This is always less than the chemical's pure-phase **solubility** in water. The effective solubility is calculated from the compound's mole fraction in the mixture and the chemical's pure phase solubility in water.

Ex-situ

Away from its native location, moved from its original place; excavated; removed or recovered from the subsurface.

From http://www.epa.gov/OUST/pubs/tum_appx.pdf

Fractionate

To separate a chemical compound into components; for example, by distillation or crystallization.

Gasoline

Gasoline is typically composed of C4 to C12 hydrocarbons, with the majority of the mass between C4 and C10. These lighter-weight hydrocarbons include **aliphatics** and **aromatics** (including **BTEX**). Minor amounts of the

Greenhouse gas

Without the “greenhouse effect,” Earth would be too cold—an estimated 30 °C (54 °F) less than current average temperatures—for life to survive. Our atmosphere, and its effective trapping of solar heat, enables plants and animals, including people, to eat and live. There are six greenhouse gases active in the planetary greenhouse effect; three of them are naturally occurring but can also be generated by human activity, and three of them are generated solely by human activity.

Naturally Occurring Gases:

- Carbon dioxide (CO_2)
- Methane (CH_4)
- Nitrous oxide (N_2O)

Industrial Gases:

- Hydrofluorocarbons (HFCs)
- Perfluorocarbons (PFCs)
- Sulfur hexafluoride (SF_6)

For more information, or to see an illustration of the natural greenhouse effect, go to:
http://tonto.eia.doe.gov/energyexplained/index.cfm?page=environment_about_ghg

Groundwater Basin

A groundwater reservoir defined by the overlying land surface and the underlying **aquifers** that contain water stored in the reservoir. Boundaries of successively deeper **aquifers** may differ and make it difficult to define the limits of the basin. (Municipal Water District of Orange County http://www.mwdoc.com/pages.php?id_pge=101)

Heavy fuel oils (lubricating oils and hydraulic oils)

Heavy fuel oils and lubricants are very similar to **middle distillate fuels,** such as **diesel,** in their composition and characteristics, except that the predominant compounds have higher molecular weights. These fuels are viscous and insoluble, and thus highly immobile in the subsurface. Lubricating oils are composed primarily of C25 to C32 hydrocarbons, which are almost exclusively **aliphatics** (branched and cyclic **alkanes**). **Aromatic** hydrocarbons are not present in lubricating oils prior to use in engines. Because of their very large molecular sizes and the fact that they are exclusively **aliphatic**, lubricating oils are nearly insoluble in groundwater, are not volatile, and pose virtually no risk to human health.

From the Fate and Transport chapter**.**

Henry’s Law Coefficient (or Constant)

This is the ratio of the vapor-phase concentration of an organic chemical relative to its dissolved-phase concentration in water. See **vapor pressure**.

Hydraulic conductivity (of soils)

Hydraulic conductivity is a quantitative measure of a saturated soil’s ability to transmit water when subjected to a hydraulic gradient. It can be thought of as the ease with which pores of a **saturated** soil permit water movement.

Based on http://soils.usda.gov/technical/technotes/note6.html

Hydrogeology

Hydrogeology involves using knowledge from both hydrology (the study of water occurrence, distribution, movement, and quality) and geology (the study of the solid earth and the processes that shape and change it) to understand how water interacts with geological systems.

From http://www.eoearth.org/topics/view/49562/

Hydrology

Hydrology is the science that encompasses the occurrence, distribution, movement, and properties of the waters of the earth (both surface and subsurface water bodies) and their relationship with the environment within each phase of the hydrologic cycle, also referred to as the WATER CYCLE.

From http://ga.water.usgs.gov/edu/hydrology.html

In-situ

In its original place; unmoved; unexcavated; remaining in the subsurface.

From http://www.epa.gov/OUST/pubs/tum_appx.pdf

Light non-aqueous-phase liquid (LNAPL), DNAPL

LNAPL is "pure product" (e.g., gasoline) that remains undiluted as the original bulk liquid in the subsurface. When petroleum is released into the environment, it is typically released as a light non-aqueous-phase liquid (LNAPL). LNAPLs (including **gasoline**, **diesel**, and other fuels, most crude oils, and creosote) are less dense than water, while *dense* non-aqueous phase liquids (such as many chlorinated solvents) are more dense than water. This Manual discusses LNAPLs only, as these are petroleum-hydrocarbon based.

Lower Explosive Limit (LEL)

The Flammable Range (Explosive Range) is the range of a concentration of a gas or vapor that will burn (or explode) if an ignition source is introduced.

Below the explosive or flammable range, the mixture is too lean to burn; above the upper explosive or flammable limit, the mixture is too rich to burn. The limits are commonly called the "Lower Explosive or Flammable Limit" (LEL/LFL) and the "Upper Explosive or Flammable Limit" (UEL/UFL).

From http://www.engineeringtoolbox.com/explosive-concentration-limits-d_423.html ,
which also provides a table of LELs and UELs for many common gases, expressed as a percent gas.

Mass spectrometry

Mass spectrometry (MS) is an analytical technique for the determination of the elemental composition of a sample or molecule. It is also used for elucidating the chemical structures of molecules. The MS principle consists of ionizing chemical compounds to generate charged molecules or molecule fragments and measurement of their mass-to-charge ratios. In a typical MS procedure:

1) a sample is loaded onto the MS instrument, and undergoes vaporization,
2) the components of the sample are ionized by one of a variety of methods (e.g., by impacting them with an electron beam), which results in the formation of positively charged particles (ions),
3) the positive ions are then accelerated by an electric field,
4) computation of the mass-to-charge ratio (*m/z*) of the particles based on the details of motion of the ions as they transit through electromagnetic fields, and
5) detection of the ions, which in step 4 were sorted according to *m/z*.

More detail on steps 4 and 5: The streams of sorted ions pass from the analyzer to the detector, which records the relative abundance of each ion type. This information is used to determine the chemical element composition of the original sample.
From http://en.wikipedia.org/wiki/Mass_spectrometry

Maximum Contaminant Levels (MCLs)

Maximum Contaminant Levels (MCLs) are maximum concentration levels allowed by law in public water supplies promulgated by the State of California Department of Public Health and published in Titles 17 and 22 of the *California Code of Regulations* (CCR).

Methanogenesis, methanogenic

The fermentation by **micro-organisms** of simple organic carbon compounds or oxidation of H_2 under **anaerobic** (without oxygen) conditions with the production of CH_4 and CO_2. Methanogenic conditions prevail in many contamination plumes after all other electron acceptors (O_2, NO_3, Fe^{+3}, and SO_4) have been used up by other members of the subsurface microbial community.

From http://toxics.usgs.gov/definitions/methanogenesis.html

Micro-organisms

Soil normally contains large numbers of diverse micro-organisms, including bacteria, algae, fungi, protozoa, and actinomycetes. Many of these micro-organisms assist in the processes of **natural attenuation** and/or **biodegradation**.

Middle-weight hydrocarbons, middle distillate fuels

See **Diesel.**

Mole fraction

The **mole fraction** is the number of moles of a given compound divided by the total number of moles of all compounds in the given solution or gas. The mole fraction is used to estimate the compound's effective solubility (maximum dissolved-phase concentration) or maximum vapor-phase concentration.

The mole fraction of compound *i* in a TPH mixture (such as LNAPL), *x*, is calculated from

$$x = \frac{C_i \cdot MW_{TPH}}{MW_i \cdot C_{TPH}}$$

where

MW_{TPH}= average molecular weight of the hydrocarbon mixture (or product) [g/mol]
MW_i = molecular weight of component *i* [g/mol]
C_{TPH} = TPH concentration (usually measured in as total concentration in soil) [g/g]
C_i = concentration of component *i* in the mixture (usually measured as total concentration in soil) [g/g]

Monitoring well

A well constructed exclusively to monitor and/or sample conditions of a water-bearing **aquifer**, e.g., water pressure, depth, movement, temperature, or quality.

Natural attenuation

Natural-attenuation processes include a variety of physical, chemical, or biological processes that, under favorable conditions, act without human intervention to reduce the mass, toxicity, mobility, volume, and/or concentration of contaminants in soil or groundwater. These processes include **biodegradation**, dispersion, dilution, volatilization, and chemical or biological stabilization, transformation, or destruction of contaminants.
From http://www.epa.gov/oust/directiv/d9200417.pdf

Non-detectable concentrations(s)

Chemicals that are not detected in a sample above a certain limit, usually the quantitation limit for the chemical in the sample. See **Detection Limits.**

Organoleptic

Of or pertaining to the sensory properties of a chemical, such as taste and odor. For example, the California MCL for MTBE is based on organoleptic properties rather than its toxicity.

Over-excavation

Over-excavation is any additional excavation needed after a UST and the surrounding soil have been removed. Confirmation samples are usually collected from the walls and floor of the excavation pit and sent for laboratory analysis to ensure that the remaining soil does not present a threat to groundwater. However, if the analytical results of the soil samples reveal unexpectedly high concentrations of targeted analytes, or perhaps the presence of unexpected analytes, over-excavation may be appropriate.

Owner, operator

"Owner" is defined in the California Health and Safety Code as the owner of an UST; "operator" is defined as any person in control of, or having daily responsibility for, the daily operation of a UST. The owner/operator is usually the **responsible party (RP)** at a LUFT site.

From California H&SC §25281.

Oxidation/reduction ("redox") reaction

Redox reactions (the common name for oxidation-reduction reactions) generate the energy required in order for biodegradation to occur; they are fundamentally a set of reactions explaining the transfer of electrons between compounds. *Oxidation* is the half-reaction involving the loss of electrons, and *reduction* is the half-reaction involving the gain of electrons. These reactions are always paired–oxidation and reduction happen virtually simultaneously.

In the context of **biodegradation**, the important thing to remember about redox reactions is that these reactions are needed to release energy to be used for microbial growth. The more energy derived from a redox reaction, the faster **micro-organisms** utilizing that reaction can grow.

From the Fate and Transport chapter.

Oxygenate

Oxygenates are fuel additives (alcohols and ethers) that contain oxygen, which can boost gasoline's octane quality, enhance combustion, and reduce exhaust emissions. In California, the term "oxygenated gasoline" most commonly refers to the type of gas sold during wintertime in order to reduce emissions of carbon monoxide (CO) from motor vehicles.

From http://www.epa.gov/OMS/oxygenate.htm).

Physico-chemical properties

This is a short-hand phrase used to refer to the physical and chemical properties of a given chemical or compound. Physico-chemical properties can include, but aren't limited to, aqueous solubility, vapor pressure, density, the **Henry's Law Constant**, specific gravity, and biodegradability. These properties are needed to evaluate the fate and transport of the chemical.

Plan-view site map

Plan view is sometimes also referred to as BIRD'S-EYE VIEW. A site map in plan view shows all current and salient former features of the site.

Polycyclic aromatic hydrocarbons (PAHs)

PAHs are chemical compounds that consist of fused **aromatic** rings. They are of concern because some compounds have been identified as carcinogenic, mutagenic, and/or teratogenic and therefore have high toxicity values.

Receptor

A receptor is a human or other living organism with the potential to be exposed to and adversely affected by contaminants because it is present at the source or along the contaminant migration pathway.

From the Conceptual Site Model chapter.

Responsible party (RP)

The party (or parties) responsible for the LUFT site. Usually the RP is the site owner or operator. (See **Owner, operator**.) Sometimes the RP(s) can include former owners of the site or the party supplying the fuel.

Saturated zone

The subsurface zone in which all the voids (spaces between particles of rock/soil) in the rock or soil are filled with water. The water table is the top of the saturated zone in an unconfined **aquifer**.

Smear zone

The smear zone is the area where free product, which settled on the water table, has been transported, or "smeared," through soils due to a seasonally fluctuating water table. The smear zone is defined as a zone in soil, regardless of whether that soil is above or below the water table at any given time.

Solubility

Solubility is the measure of the ability of a chemical to dissolve in water. See **Effective solubility**.

From the Fate and Transport chapter.

Speciated

Analytical activity of identifying and/or measuring the specific forms of an element (such as a metal) defined as to isotopic composition, electronic or oxidation state, and/or complex or molecular structure. For example, determining the amount of methyl lead ***vs.*** inorganic lead in a soil sample.

From http://www.speciation.net/Public/Document/2003/09/11/495.html.

Stakeholders

All parties with a direct or indirect interest in the outcome of an activity are stakeholders in that activity.

Stratigraphy

Usually a description of the rock or soil strata in the subsurface, particularly the sequences of layers.

From http://topex.ucsd.edu/erth01/Glossary.html

Total dissolved solids (TDS)

Total dissolved solids (TDS) refers to the amount of inorganic materials such as minerals, salts, metals, cations, or anions dissolved in water. TDS is usually a measurement of the inorganic salts (principally calcium, magnesium, potassium, sodium, bicarbonates, chlorides, and sulfates) present in water.

From http://www.water-research.net/totaldissolvedsolids.htm

Unauthorized release

A release of petroleum into the environment (i.e., it escapes from the secondary containment, or from the primary containment, if no secondary containment exists).

From California H&SC §25295.

Unsaturated zone

The zone between the ground surface and the aquifer's **water table** within which the moisture content is less than saturation and the pressure is less than atmospheric. In addition to water, the soil pore spaces in the unsaturated zone contain air or other gases. For an illustration, see the Fate and Transport chapter.

From: http://www.epa.gov/OUST/pubs/tum_appx.pdf

Vadose zone

The vadose zone is the **unsaturated zone**.

Vapor Pressure

Vapor pressure or equilibrium vapor pressure is the pressure of a vapor in thermodynamic equilibrium with its liquid or solid forms in a closed container. The equilibrium vapor pressure is an indication of a liquid's evaporation rate. A substance with a high vapor pressure at normal temperatures is often referred to as “volatile.” See **Henry’s Law Coefficient**.

Volatile organic compound(s) (VOCs)

Volatile organic compounds (VOCs) are organic chemical compounds with sufficiently high **vapor pressures** or **Henry’s Law Coefficients** under normal conditions to significantly volatilize and enter the gaseous phase. The BTEX chemicals are VOCs.

Water Quality Objectives (WQOs)

Narrative or numerical criteria designed to define appropriate levels of environmental quality and to control activities that can adversely affect aquatic systems.

Chapter 20: Acronyms

September 2012

Scope of This Chapter

This is a complete list of acronyms in the California LUFT Manual, with their full spellings.

Every field has its own abbreviations and acronyms, and LUFT investigations and their participating disciplines are no exception. Each term below has been fully spelled out when it first appears in a chapter, and is afterwards used only in its shortened form. The table below also references where the acronym was first referenced.

Acronym	Definition	First Referenced Chapter
µg/L	Micrograms per liter	8: Reports
µg/L-vapor	Micrograms per liter – vapor	15: Site Assessment
µg/m^3	Micrograms per cubic meter	Appendix C: Vapor Intrusion
AB	Assembly bill	3: UST Cleanup Fund
AFCEE	Air Force Center for Engineering and the Environment	18: Remediation
AHA	Activity Hazard Analysis	5: Health and Safety
APCD	Air pollution control district	5: Health and Safety
APH	Air-Phase Petroleum Hydrocarbons	16: Laboratory Analysis and Methods
API	American Petroleum Institute	15: Site Assessment
ARCH	Air rotary casing hammer	15: Site Assessment
AS	Air sparging	18: Remediation
AST	Aboveground storage tank	14: Conceptual Site Model
ASTM	ASTM International (formerly American Society for Testing and Materials)	15: Site Assessment
atm-m^3/ mol	Atmosphere-cubic meter(s) per mole(s) [units used in calculating the Henry's Law Constant]	13: Fate and Transport
bgs	Below ground surface	14: Conceptual Site Model
BMP	Best Management Practices	5: Health and Safety
BPC	Business and Professions Code	2: Roles and Responsibilities
BTEX	Benzene, toluene, ethylbenzene, and xylenes	13: Fate and Transport
Cal/EPA	California Environmental Protection Agency	5: Health and Safety
CAP	Corrective Action Plan	2: Roles and Responsibilities
CARB	California Air Resources Board	Glossary
Case Closure Policy	Low-Threat UST Case Closure Policy (pursuant to State Water Board Resolution 2012-0016)	6: Work Plans
CCR	*California Code of Regulations*	1: Overview
CDC	Centers for Disease Control	5: Health and Safety
CEQA	California Environmental Quality Act	2: Roles and Responsibilities
cfm	Cubic feet per minute	18: Remediation
CFR	*Code of Federal Regulations*	3: UST Cleanup Fund
CFU	Colony Forming Unit	18: Remediation
CGI	Combustible gas indicator	5: Health and Safety
CHHSL	California Human Health Screening Level	17: Risk Evaluation and Risk Mgmt.
cis-1,2-DCE	cis-1,2-Dichloroethene	Appendix C: Vapor Intrusion
cm	Centimeter	Appendix C: Vapor Intrusion
CMT	Continuous multi-channel tubing system	15: Site Assessment
CO	Carbon monoxide	Glossary

Acronym	Definition	First Referenced Chapter
COCs	Constituents of concern	6: Work Plans
COELT	U.S. Army Corps of Engineers Loading Tool	4: GeoTracker
cp, cP	centipoise (also centiPoise) (unit of measurement for viscosity)	13: Fate and Transport
CPS	Cleanup Program Sites	4: GeoTracker
CPT	Cone Penetration Testing	15: Site Assessment
CSM	Conceptual Site Model	3: UST Cleanup Fund
CUPA	Certified Unified Program Agency	2: Roles and Responsibilities
CVOC	Chlorinated volatile organic compound	16: Laboratory Analysis and Methods
1,2-DCA	1,2-Dichloroethane	16: Laboratory Analysis and Methods
1,1-DCE	1,1-Dichloroethene	Appendix C: Vapor Intrusion
DFA	Division of Financial Assistance (State Water Board)	3: UST Cleanup Fund
DHS	California Department of Health Services	1: Overview
DIPE	di-Isopropyl ether	13: Fate and Transport
DO	Dissolved oxygen	15: Site Assessment
DoD	Department of Defense	4: GeoTracker
DPE	Dual-phase extraction	18: Remediation
DPT	Direct-push technologies	15: Site Assessment
DQO	Data quality objective	8: Reports
DRO	Diesel-range organics (C10 to C16 and C17 to C25)	13: Fate and Transport
DTSC	State of California Dept. of Toxic Substances Control	15: Site Assessment
DWR	California Department of Water Resources	14: Conceptual Site Model
EC	Equivalent carbon number	13: Fate and Transport
EC	Electrical conductivity	18: Remediation
ECD	Electron capture detector	16: Laboratory Analysis and Methods
EDB	Ethylene dibromide (aka 1,2-Dibromoethane)	13: Fate and Transport
EDC	Ethylene dichloride (aka 1,2-DCA = 1,2-Dichloroethane)	13: Fate and Transport
EDD	Electronic data deliverable	4: GeoTracker
EDF	Electronic Deliverable Format™	4: GeoTracker
Eh	Reduction potential	15: Site Assessment
ELAP	Environmental Laboratory Accreditation Program	6: Work Plans
EM	Electromagnetic Induction	15: Site Assessment
EPA	(U.S.) Environmental Protection Agency	1: Overview
EPH	Extractable petroleum hydrocarbon	16: Laboratory Analysis and Methods
ESA	Expedited site assessment	6: Work Plans
ESI	Electronic submittal of information	4: GeoTracker
ESL	Environmental Screening Levels	14: Conceptual Site Model
ETBE	Ethyl tert butyl ether	13: Fate and Transport
EtOH	Ethanol	13: Fate and Transport
FID	Flame ionization detector	13: Fate and Transport
Fund	3: UST Cleanup Fund	1: Overview
FY	Fiscal Year	3: UST Cleanup Fund
g/cm^3 **or** g/cc	Grams per cubic centimeter	15: Site Assessment
GAMA	Groundwater Ambient Monitoring Assessment	4: GeoTracker
GC	Gas chromatograph(y)	13: Fate and Transport
GC-ECD	Gas chromatography / Electron capture detector	16: Laboratory Analytical Methods

Acronym	Definition	First Referenced Chapter
GC-FID	Gas chromatography / Flame ionization detector	13: Fate and Transport
GC-MS	Gas chromatography / Mass spectrometry	16: Laboratory Analysis and Methods
GC-PID	Gas chromatography / Photo-ionization detector	16: Laboratory Analysis and Methods
GIF	Graphics interchange format	4: GeoTracker
GIS	Geographic information system	4: GeoTracker
GPR	Ground Penetrating Radar	15: Site Assessment
GRO	Gasoline-range organics (C4 to C10)	13: Fate and Transport
H&SC	Health & Safety Code	1: Overview
HASP	Health and Safety Plan	5: Health and Safety
HAZWOPER	Hazardous Waste Operations and Emergency Response	5: Health and Safety
HEM	*n*-Hexane extractable material	16: Laboratory Analysis and Methods
HI	Hazard index	17: Risk Evaluation and Risk Mgmt.
HML	Hazardous Materials Laboratory	16: Laboratory Analytical Methods
HMW	High molecular weight	13: Fate and Transport
HPC	Heterotrophic plate count	18: Remediation
HSA	Hollow-stem auger	15: Site Assessment
HVAC	Heating, ventilation, and air conditioning	Appendix C: Vapor Intrusion
ICs	Institutional controls	18: Remediation
IDW	Investigation-derived waste	5: Health and Safety
ISCO	In-situ chemical oxidation	18: Remediation
ITRC	Interstate Technology & Regulatory Council	14: Conceptual Site Model
JPEG, JPG	Joint Photographic Experts Group (file suffix)	4: GeoTracker
JSA	Job Safety Analysis	5: Health and Safety
LEL/LFL	Lower explosive (flammable) limit	5: Health and Safety
LIA	Local Implementing Agency	2: Roles and Responsibilities
LIF	Laser-Induced Fluorescence	15: Site Assessment
LIMS	Laboratory Information Management System	4: GeoTracker
LNAPL	Light non-aqueous-phase liquid	11: Release Response Prioritization
LOC	Letter of Commitment	3: UST Cleanup Fund
LOP(s)	Local Oversight Program(s)	2: Roles and Responsibilities
LUFT	Leaking Underground Fuel Tank	1: Overview
MADEP	Massachusetts Department of Environmental Protection	16: Laboratory Analysis and Methods
MCL	Maximum Contaminant Level	17: Risk Evaluation and Risk Mgmt.
MF	Mass fraction	13: Fate and Transport
mg/kg	Milligrams per kilogram	8: Reports
mg/L	Milligrams per liter	Appendix C: Vapor Intrusion
MIP	Membrane Interface Probe	15: Site Assessment
mL	Milliliter	16: Laboratory Analysis and Methods
mm	Millimeter	15: Site Assessment
mm Hg	Millimeters of mercury	13: Fate and Transport
MS	Mass spectrometry	16: Laboratory Analytical Methods
MSDS	Material Safety Data Sheet	5: Health and Safety
MTBE	Methyl tertiary butyl ether	13: Fate and Transport
NA, N/A	Not applicable	12: Tank Removal and Closure in Place
NAPL	Non-aqueous-phase liquid	5: Health and Safety
NFA request	No Further Action request	7: Corrective Action Plan

Acronym	Definition	First Referenced Chapter
NPDES	National Pollutant Discharge Elimination System	5: Health and Safety
N, NSOs	Heterocyclic compounds (nitrogen, sulfur, oxygen)	13: Fate and Transport
O&M	Operation and maintenance	7: Corrective Action Plan
OEHHA	Office of Environmental Health Hazard Assessment	17: Risk Evaluation and Risk Mgmt.
OR DEQ	Oregon Department of Environmental Quality	13: Fate and Transport
ORO	Oil-range organics (C25 to C32)	13: Fate and Transport
ORP	Oxidation/reduction potential	15: Site Assessment
OSHA	Occupational Safety and Health Administration	5: Health and Safety
OSWER	Office of Solid Waste and Emergency Response	9: Green and Env. Responsible Cleanups
OUST	Office of Underground Storage Tanks	Appendix C: Vapor Intrusion
Pa	Pascal (unit of atmospheric pressure)	Appendix C: Vapor Intrusion
PAHs	Polycyclic aromatic hydrocarbons	13: Fate and Transport
PDF	Portable document format	4: GeoTracker
PIANO	Paraffins, Isoparaffins, Aromatics, Naphthenes (cycloalkanes), and Olefins	16: Laboratory Analysis and Methods
PID	Photo-Ionization Detector	12: Tank Removal and Closure in Place
PLC	Programmable logic controller	18: Remediation
POTW	Publicly owned treatment works	7: Corrective Action Plan
PPE	Personal protective equipment	5: Health and Safety
ppm	Parts per million	18: Remediation
ppm(v)	Parts per million by volume	15: Site Assessment
PRGs	Preliminary Remediation Goals	17: Risk Evaluation and Risk Mgmt.
psig	Pounds per square inch gauge	18: Remediation
PVC	Polyvinyl chloride	15: Site Assessment
QA	Quality assurance	4: GeoTracker
QC	Quality control	6: Work Plans
RAGS	Risk Assessment Guidance for Superfund	17: Risk Evaluation and Risk Mgmt.
RBCA	Risk-based corrective action	13: Fate and Transport
RCRA	Resource Conservation and Recovery Act	10: Initial Reporting
redox	Oxidation-reduction	15: Site Assessment
RfD	Reference dose	13: Fate and Transport
ROI	Radius of influence	18: Remediation
ROST	Rapid Optical Screening Tool	15: Site Assessment
RP	Responsible Party	1: Overview
RSLs	Regional Screening Levels	13: Fate and Transport
Regional Water Boards	Regional Water Quality Control Board	2: Roles and Responsibilities
SAM	Site Assessment and Mitigation	12: Tank Removal and Closure In Place
SB	Senate Bill	3: UST Cleanup Fund
SC	Site Cleanup	4: GeoTracker
scfm	Standard cubic feet per minute	18: Remediation
SESD	Science and Ecosystem Support Division	15: Site Assessment
SGC	Silica-gel cleanup	13: Fate and Transport
SIM	Single Ion Monitoring	16: Laboratory Analysis and Methods
SLIC	Spills, Leaks, Investigations, and Cleanups	4: GeoTracker

Acronym	Definition	First Referenced Chapter
SOP	Standard operating procedure	6: Work Plans
SOW	Scope of work	6: Work Plans
SPH	Separate-phase hydrocarbons	15: Site Assessment
SPT	Standard Penetration Test	15: Site Assessment
SSD	Sub-slab depressurization system	Appendix C: Vapor Intrusion
State Water Board	State Water Resources Control Board	1: Overview
SVE	Soil-vapor extraction	11: Release Response Prioritization
SVOC	Semi-volatile organic compound	18: Remediation
TAME	Tertiary amyl methyl ether	13: Fate and Transport
TBA	*t*-Butyl alcohol	13: Fate and Transport
TCLP	Toxicity Characteristic Leaching Procedure	16: Laboratory Analysis and Methods
TEL	Tetra ethyl lead (also “tetra ethyllead”)	13: Fate and Transport
TIC	Tentatively identified compound	16: Laboratory Analysis and Methods
TIFF	Tagged image file format	4: GeoTracker
TMB	Trimethylbenzene	13: Fate and Transport
TML	Tetra methyl lead (also “tetra methyllead”)	13: Fate and Transport
TOG	Total oil and grease	16: Laboratory Analysis and Methods
TPH	Total petroleum hydrocarbons	13: Fate and Transport
TPHCWG	Total Petroleum Hydrocarbons Criteria Working Group	13: Fate and Transport
TPHd/mo	Total petroleum hydrocarbons as diesel or motor oil	13: Fate and Transport
TRPH	Total recoverable petroleum hydrocarbons	16: Laboratory Analysis and Methods
TSD	Treatment, storage, and disposal	12: Tank Removal and Closure In Place
UCL	Upper confidence limit	17: Risk Evaluation and Risk Mgmt.
UEL/UFL	Upper explosive (flammable) limit	Glossary
USA	Underground Service Alert	12: Tank Removal and Closure In Place
USCG	U.S. Coast Guard	5: Health and Safety
USCS	United Soil Classification System	15: Site Assessment
USGS	U.S. Geological Survey	15: Site Assessment
UST	Underground storage tank	1: Overview
USTCF	UST Cleanup Fund	3: UST Cleanup Fund
VI	Vapor intrusion	Appendix C: Vapor Intrusion
VOA	Volatile Organic Analysis	16: Laboratory Analysis and Methods
VOC	Volatile organic compound	12: Tank Removal and Closure In Place
VPH	Volatile petroleum hydrocarbon	16: Laboratory Analysis and Methods
VVLs	Valid Value Lists	4: GeoTracker
WC	(California) Water Code	4: GeoTracker
WDR	Waste Discharge Requirement	4: GeoTracker
WQOs	Water Quality Objectives	14: Conceptual Site Model
WSF	Water soluble fraction	13: Fate and Transport

CALIFORNIA LUFT MANUAL

APPENDIX A

LOW–THREAT UST CASE CLOSURE POLICY:

TECHNICAL JUSTIFICATION DOCUMENTS

- Technical Justification for Soil Screening Levels for Direct Contact and Outdoor Air Exposure Pathways
- Technical Justification for Groundwater Media-Specific Criteria
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Technical Justification for Soil Screening Levels for Direct Contact and Outdoor Air Exposure Pathways

(Final 03-15-2012)

1 EXECUTIVE SUMMARY

Soil screening levels have been proposed to be used in conjunction with vapor intrusion criteria and groundwater criteria for identifying sites posing a low-threat to human health. That is, these soil screening levels are just one of three sets of criteria that should be evaluated to determine if a site is low-threat.

The soil screening levels discussed in this document have been developed for benzene, ethylbenzene, naphthalene, and polyaromatic hydrocarbons (PAHs). The exposure pathways considered in the conceptual site model are: **incidental ingestion of soil, dermal contact with soil, and inhalation of dust and volatile emissions from soil.** Note these exposure pathways are assumed to occur simultaneously, i.e., the screening levels are protective of exposure from all four exposure pathways for each chemical. Standard U.S. EPA risk assessment equations were used to derive the screening levels. The exposure parameter values, chemical toxicity values, and chemical fate and transport properties are based on default values used in California.

Risks posed by direct exposure to multiple chemicals with similar health effects are considered to be additive or cumulative. For example, the total risk posed by the presence of carcinogenic chemicals is the sum of the theoretical risk posed by each individual chemical. The same is true for chemicals that cause noncarcinogenic health effects. Use of these screening levels for single chemicals is limited to the extent that the screening levels remain protective of human health should other chemicals with similar health effects are present. Assuming all four chemicals are present at the same location and at concentrations at their respective screening levels, the estimated total risk is 4×10^{-6}. For reference, the USEPA National Contingency Plan (NCP) is commonly cited as the basis for acceptable risks in risk management decisions. According to the NCP, an acceptable site-specific lifetime incremental cancer risk falls with the range of 1 in a million (1×10^{-6}) to 100 in a million (1×10^{-4}). Cancer risks below or within the range of 10^{-6} to 10^{-4} are generally considered protective of human health by the USEPA. The estimated total risk for the four chemicals considered in this document (4×10^{-6}) falls within this range.

Two sets of screening levels were developed for two soil horizons: one from 0 to 5 feet below ground surface (bgs) and one from 5 to 10 feet bgs[1] and three exposure scenarios (residential,

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[1] There are several definitions of what constitutes surface soil ("near" surface soil is typically the top 6 inches of soil) to quantify potential exposures in health risk assessments. Surface soil can be defined as soil to a depth of 2 feet below ground surface

commercial/industrial, and a utility trench worker) were considered. This document describes the technical background for the development of the soil screening levels.

2 INTRODUCTION

The equations used to develop the soil screening levels are identical to the equations used to derive the USEPA's Regional Screening Levels (RSLs; USEPA 2011). Exposure parameter values were assumed to equal the default values used in California Department of Toxic Substances (DTSC) Office of Human and Ecological Risk (HERO) "Human Health Risk Assessment (HHRA) Note Number 1" (DTSC 2011). The soil screening levels presented in this document are sufficiently protective because the assumptions used to calculate the values are based on conservative assumptions and exposures.

The volatilization factor used in the RSLs was replaced with volatilization factors obtained from the American Society of Testing Material's (ASTM's) Standard Guide for Risk-Based Corrective Action Applied at Petroleum Release Sites (ASTM 1995). The ASTM volatilization factors used to calculate concentrations in outdoor air consider mass balance. The volatilization algorithm used in the RSLs can overestimate the amount of contaminant volatilizing into outdoor air (Cal/EPA, 2005). In the ASTM volatilization algorithm[2], if the calculated volatilization rate depletes the source before the end of the exposure duration, the volatilization rate is adjusted so that the total source mass is assumed to volatilize by the end of the exposure duration. By using this mass-balance check, it is ensured that the total amount volatilized does not exceed the total amount of contaminant in soil.

For incidental ingestion of soil, dermal contact with soil, and inhalation of dust, the concentration in soil is assumed to be constant at the screening level for the entire exposure duration. This assumption is conservative for volatile chemicals or chemicals that are expected to biodegrade in soil, such as benzene and ethylbenzene.

2.1 Screening Levels vs. Risk

The soil screening levels represent concentrations, below which, indicate the site is a low-threat risk for human health. Multiple conservative assumptions were made when developing these soil screening levels. Actual site risk is expected to be lower than the risk targets used to develop the screening levels. For example, a residential receptor is assumed to come into contact with soil at concentrations

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or as indicated in the supporting documentation for the CHHSLs and ESLs, a depth of approximately 10 feet is generally used to delineate between shallow soil, where a potential exists for regular direct contact, and deep soil where only periodic exposure is considered likely.

[2] The ASTM VF differs from the approach used by USEPA in the development of the RSLs. The VF used to calculate the RSLs assumes infinite sources over a large source area for the dispersion term. The ASTM VF algorithm is considered more appropriate for leaking underground fuel tank (LUFT) sites. Further details on the differences are presented in the Draft California LUFT Guidance Manual, version 2.0, 2010).

equivalent to the screening level every day (350 days/year) for a total of 30 years. While most residential exposures would not occur at the default levels used to derive these screening levels, the defaults are designed to be protective for this hypothetical scenario.

Note that site concentrations that exceed the screening levels do not indicate unacceptable human health risks with regards to these pathways; rather, an exceedance may indicate that a site-specific evaluation of human health risk is warranted.

2.2 Chemicals Considered

Risk-based soil screening levels were developed for benzene, ethylbenzene, naphthalene and PAHs. These constituents are considered the primary risk-driving compounds at petroleum-impacted sites.

Total petroleum hydrocarbons (TPH) were not considered as a chemical of concern. The stakeholders chose not to include TPH in policy for the following reasons:

- TPH consists of a mixture of more than 2000 chemicals.
- Once in soil, the TPH starts weathering immediately changing its composition through time and from one site to the next.
- Bulk TPH measurements, such as those obtained by analytical method 8015M, are not suitable for risk assessment because they do not provide information about the composition with respect to chemical toxicity and fate and transport properties.
- None of the regulatory agencies in California that are responsible for requiring risk assessment have an approved analytical method for evaluating TPH for purposes of risk assessment (such as a fractionation method). In fact, most analytical labs in California are not familiar with TPH fractionation.
- Benzene, ethylbenzene and naphthalene more accurately capture the risk that TPH poses for human health concerns.

Methyl tert-butyl ether (MTBE) was not considered as a chemical of concern for the following reasons:[3]

> *For benzene, the USEPA RSL in soil for residential land use is 1.1 mg/kg, which is approximately 1,650-times lower than its soil saturation concentration. For MTBE, the residential soil RSL is 43 mg/kg, which is about 200-times lower than its soil saturation concentration. Even though the MTBE content of gasoline may be 10- to 15-times that of benzene, potential risks from direct contact with soil will still be driven by benzene, which is about 60-times more toxic than MTBE. Currently, USEPA does not evaluate MTBE as a potential human carcinogen. The State of California has developed a cancer slope factor for MTBE based on a combination of data from two animal studies, one study by the inhalation route and the other study by the oral route. Numerous*

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[3] Written communication with the Department of Toxic Substances Control, Human and Ecological Risk Office.

uncertainties have been identified in the animal studies, including severe mortality and lack of histopathological criteria. In addition, the mechanism of MTBE carcinogenicity is not known. Given the uncertainties associated with MTBE carcinogenicity, benzene will be the risk-driving chemical of concern associated with fuel-related hydrocarbons, especially considering that benzene is a known human carcinogen with a known mechanism of action.

The soil screening level for "PAH" is appropriate for comparison with the total concentration of the seven carcinogenic PAHs, as benzo(a)pyrene equivalents (BaPe)[4]. The carcinogenic PAHs typically analyzed during site investigations are: benz[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, chrysene, dibenz(a,h)anthracene, and indeno(1,2,3-cd)pyrene. The toxicity value used for the entire group of carcinogenic PAHs is California's Office of Environmental Health Hazard Assessment (OEHHA) cancer potency value for benzo(a)pyrene (OEHHA 2010). This is a conservative assumption because the few PAHs that are more carcinogenic than benzo(a)pyrene are typically not found in petroleum mixtures.

2.3 Requirements for Using Screening Levels

There is only one "model" used in calculation of the Screening Levels. This model assumes the following:

- The area of impacted soil where a particular exposure occurs is 25 by 25 meters (approximately 82 by 82 feet) or less. This does not mean that the site or the property has to be less than 25 by 25 meters. If the area of impacted soil where a particular exposure is larger, a site-specific risk analysis may be warranted.
- The receptor is located at the downgradient edge for inhalation exposure. For residential exposures, it is assumed that the receptor is located on site for 24 hours/day for the entire exposure duration. For industrial and utility workers, it is assumed that the worker is located onsite for 8 hours/day.
- The wind speed is assumed to equal 2.25 meters per second (m/s) on average. If the average wind speed is lower, a site-specific risk analysis may be warranted.
- The default input parameters for all exposure scenarios were obtained from DTSC defaults for California hazardous waste sites. If the exposure scenarios are different, a site-specific risk analysis may be warranted.

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[4] The Office of Environmental Health Hazard Assessment (OEHHA) of Cal/EPA has developed potency equivalency factors (PEFs) for carcinogenic PAHs based on their potential toxicity when compared to benzo(a)pyrene [B(a)P]. To estimate B(a)P toxicity equivalents (TEQs; referred to as BaPe), the concentration of each carcinogenic PAH detected in soil is multiplied by the appropriate PEF developed by OEHHA [benz[a]anthracene (0.1), benzo[a]pyrene (1.0), benzo[b]fluoranthene (0.1), benzo[k]fluoranthene (0.1), chrysene (0.01), dibenz(a,h)anthracene (0.34), and indeno(1,2,3-cd)pyrene (0.1). The sum of BaPe concentrations for a mixture of PAH results in a total BaPe for each sample; the total BaPe concentrations should be compared to the soil screening level for PAHs.

3 CONCEPTUAL SITE MODEL

This section describes the exposure scenarios and receptors considered in the development of the soil screening levels. Soil screening levels were developed for two different soil horizons. A schematic of the conceptual site model for the two soil horizons is shown in Figure 1.

3.1 Exposure Pathways

The soil screening levels consider four exposure pathways simultaneously:

- incidental ingestion of soil;
- dermal contact with soil;
- inhalation of volatile soil emissions; and
- inhalation of particulate emissions.

Incidental ingestion of and dermal contact with soil are direct exposure pathways, i.e., the receptor is assumed to contact the soil directly and, therefore, the exposure point concentration is the actual concentration in soil. For the inhalation exposure pathways, the exposure medium is outdoor air; the outdoor air concentration must be estimated using volatilization and particulate emission factors.

3.2 Receptors Considered

Soil screening levels were calculated for three exposure scenarios. The exposure scenarios considered were:

- residential;
- commercial/industrial worker; and
- a worker in a utility trench or similar construction project (utility worker).

It is assumed that all four of the exposure pathways (discussed in section 3.1) are potentially complete for each scenario. However, the input parameter values are different for each receptor.

For the residential exposure scenario, it is assumed that the receptor is a child for 6 years and then an adult for 24 years. When calculating carcinogenic risk, the total intake of a chemical over a lifetime is used; therefore, the carcinogenic residential screening levels are protective of the combined child plus adult scenario. For benzo(a)pyrene (PAHs), the mutagenic exposure equations are used for calculating the screening level. In this case, the early life exposures (i.e., 0 to 2 years, 2 to 6 years and 6 to 16 years) are weighted more than they are in the non-mutagenic equations (Table 1). For noncarcinogenic health effects, the intake is not added over the exposure period. In this case, the child is the more sensitive receptor; therefore the noncarcinogenic screening levels are developed for a child receptor and are protective for the adult resident.

The commercial/industrial exposure scenario assumes that the receptor is an adult and works in an office or outdoors at a site. In this scenario, it is assumed that the receptor works for a total of 25 years at 250 days/year at the same location.

For the utility or construction worker, the exposure duration is assumed to be much shorter than in the other two scenarios (1 year); however, the chemical intake per day is assumed to be higher due to increased incidental ingestion and/or increased inhalation rates.

3.3 Depths to Which the Screening Levels Apply

Two sets of screening levels were developed for the residential and commercial/industrial scenarios based on depth of impacted soil: one set applies to 0 to 5 feet bgs and the other set applies to 5 to 10 feet bgs. The full depth of 0 to 10 feet is assumed to contribute to outdoor air concentrations for all scenarios.

For the residential and commercial/industrial exposure scenarios, it is assumed that residents and commercial workers could contact soil at depths between ground surface and 5 feet bgs. For the utility or construction worker, it is assumed that direct contact with soil could occur at depths between ground surface and 10 feet bgs.

4 DERIVATION OF SCREENING LEVELS

This section describes how the soil screening levels were calculated. Except the volatilization term, standard equations from the USEPA RSLs were used. A target risk level of 1×10^{-6} for carcinogens and a target hazard index of 1.0 for noncarcinogens were used.

4.1 Equations Used

4.1.1 Exposure Equations

The equations used to develop the soil screening levels are presented in Tables 1 through 3 for each receptor. The variable definitions are presented in Table 4. USEPA considers the carcinogenic PAHs to be “mutagens” and as such, has unique equations to calculate screening levels. The mutagenic equations are for “early life exposures” and therefore only apply to the residential scenario.

4.1.2 Volatilization Factor

The volatilization factor (VF) used to predict an outdoor air concentration due to volatilization from the soil is based on the ASTM guidance (1995). The assumptions in the ASTM volatilization factor algorithm (ASTM 1995) are:

- Dispersion in air is modeled from a ground-level source. It is assumed that the air in the outdoor air "box" is well-mixed;
- The receptor is located onsite, directly over the impacted soil, 24 hours/day for the entire exposure duration; and
- A long-term average exposure point concentration is estimated for the entire exposure duration.

The conceptual model for volatile emissions and inhalation of outdoor air is shown in Figure 2. The assumed receptor location at the edge of the downwind side of the source is the most conservative location that could be used. The dispersion of contaminant in the air, or mixing, is limited to the height of the breathing zone; that is, upward vertical dispersion (i.e., dilution), as the air blows towards the receptor, is not considered in the model.

The ASTM VF is actually composed of two equations as presented in Table 5: one equation assumes an infinite source, and the other one equation includes a mass balance check to limit the volatilization term so that the amount volatilized cannot exceed the total amount of mass in the soil initially. The VF is calculated using both equations and the lower of the two volatilization rates is used for the VF in the exposure equations. The default input values are presented in Table 6. Unless there are site-specific conditions, reasonable estimates for the length and width of the source are 25 meters each (approximately 82 by 82 feet). The thickness of impacted soil is assumed to equal 3.05 meters (10 feet).

4.1.3 Particulate Emission Factor

A particulate emission factor (PEF) is used to estimate the outdoor air concentrations due to chemicals airborne on particulates (dust). The default value used for the PEF for the residential and commercial/industrial scenarios is 1.3×10^9 [(mg/kg)/(mg/m^3)] (DTSC 2011). For the utility trench (construction) worker, a PEF value of 1×10^6 [(mg/kg)/(mg/m^3)] was used (DTSC 2011).

4.2 Exposure Parameter Values Used

All of the default exposure parameters for the receptors were obtained from DTSC's "Human Health Risk Assessment (HHRA) Note Number 1" (DTSC 2011). Table 4 presents the default values for each parameter and provides the reference document where each parameter value was obtained.

4.2.1 Ingestion of Soil

Receptors working or playing outdoors may ingest soil through incidental contact of the mouth with hands and clothing. For the residential and commercial exposure scenarios, one of the very conservative assumptions made is that the chemical concentrations remain constant over time in the soil. In reality, this would not be the case, especially for volatile chemicals in the top few feet of soil, where most of the direct contact would occur. Benzene, ethylbenzene and naphthalene are highly fugitive in surface soil, quickly depleting the upper soil depths.

4.2.2 Dermal Contact with Soil

Some soil contaminants may be absorbed across the skin into the bloodstream. Absorption will depend upon the amount of soil in contact with the skin, the concentration of chemicals in soil, the skin surface area exposed, and the potential for the chemical to be absorbed across the skin. Note, USEPA assumes that benzene and ethylbenzene will not be on the skin long enough (due to volatilization) to absorb through the skin.

4.2.3 Inhalation of Volatile and Particulate Emissions in Outdoor Air

The inhalation exposure route includes the inhalation of both volatile and particulate emissions. The inhalation slope factors and noncarcinogenic inhalation reference doses are presented in Table 7.

4.3 Chemical Parameter and Toxicity Values Used

The default chemical parameter values came from the RWQCB 2 Environmental Screening Levels (2007). The toxicity values for noncarcinogenic toxicity came from USEPA's On-line Risk Information System (IRIS, 2011). The carcinogenic toxicity values for benzene, ethylbenzene, and naphthalene came from OEHHA's list of cancer potency factors (OEHHA 2009). The carcinogenic oral slope factor for benzo(a)pyrene came from OEHHA's Public Health Goals for Chemicals in Drinking Water for Benzo(a)pyrene (OEHHA 2010).

5 SOIL SCREENING LEVELS

Table 8 shows the soil screening levels calculated for each exposure scenario.

Table 8: Summary of Soil Screening Levels for different Exposure Scenarios and Receptors

Chemical	Residential		Commercial/ Industrial		Utility Worker
	0 to 5 feet bgs mg/kg	Volatilization to outdoor air (5 to 10 feet bgs) mg/kg	0 to 5 feet bgs mg/kg	Volatilization to outdoor air (5 to 10 feet bgs) mg/kg	0 to 10 feet bgs mg/kg
Benzene	1.9	2.8	8.2	12	14
Ethylbenzene	21	32	89	134	314
Naphthalene	9.7	9.7	45	45	219
PAH*	0.063**	NA	0.68	NA	4.5

Notes:

* Based on the seven carcinogenic PAHs as benzo(a)pyrene toxicity equivalent [BaPe]. The PAH screening level (applicable to total BaPe) is only applicable where soil was affected by either waste oil and/or Bunker C fuel.

** DTSC (2009) reports average ambient PAH concentrations (as BaPe) in California ranging from 0.16 to 0.21 mg/kg, and upper tolerance limits (UTLs) ranging from 0.9 to 1.5 mg/kg. The screening level shown in this table is "risk-based" and is far below the average ambient concentrations for PAHs in California. It is suggested that DTSC citation (2009) be consulted for sites with PAH contamination.

NA = Not Applicable

Note, the screening levels for naphthalene are the same for the top 5 feet and for 5 to 10 feet bgs based on volatilization to outdoor air. This is because naphthalene is only carcinogenic from the inhalation exposure pathway and not from oral or dermal contact. The screening levels based on carcinogenic mode of action and inhalation were the most conservative (i.e., the carcinogenic screening levels were less than the noncarcinogenic screening levels).

6 APPLYING SOIL SCREENING LEVELS

The maximum concentrations of petroleum constituents in soil should be compared to those listed in Table 8 for the specified depth bgs and the receptor scenario. The concentration limits for 0 to 5 feet bgs are protective for ingestion of soil, dermal contact with soil, inhalation of volatile soil emissions, and inhalation of particulate emissions, and the 5 to 10 feet bgs concentration limits are protective for inhalation of volatile soil emissions in outdoor air. Both the 0 to 5 feet bgs concentration limits and the 5 to 10 feet bgs concentration limits for the appropriate site classification (residential or commercial/industrial) shall be satisfied. In addition, if exposure to construction workers or utility trench workers is reasonably anticipated, the concentration limits for the utility worker shall also be satisfied.

7 DISCUSSION

This document has presented soil screening levels to be used to identify sites that are low threat to human health risk for the direct contact pathways from impacted soil. These soil screening levels are designed to be used in conjunction with the Vapor Intrusion Criteria and Groundwater Criteria to determine if the site is a low-threat from all exposure pathways.

OEHHA has indicated that the residential exposure scenario is protective for other sensitive uses of a site. This means that these screening levels are also appropriate for other sensitive uses of the property (e.g., day-care centers and hospitals; OEHHA 2005).

8 REFERENCES

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TABLES

Table 1: Equations Used to Develop Soil Screening Levels for the Direct Contact Pathways for a Residential Exposure Scenario

(page 1 of 3)

Carcinogenic – Residential

Incidental ingestion of soil

$$SL_{res-sol-ca-ing} = \frac{TR \times AT_{Carc} \times 365\, d/yr}{SF_o \times EF_r \times IFS_{adj} \times 1\text{E}{-6}\ kg/mg}$$

where

$$IFS_{adj} = \left[\frac{ED_c \times IRS_c}{BW_c} + \frac{ED_a \times IRS_a}{BW_a} \right]$$

Inhalation of particulates and volatiles

$$SL_{res-sol-ca-inh} = \frac{TR \times AT_{Carc} \times 365\, d/yr}{IUR \times \left(\frac{1000\, \mu g}{mg} \right) \times EF_r \times \left(VF_r + \frac{1}{PEF_r} \right) \times \left(ED_c + ED_a \right) \times ET_r \times \left(\frac{1\ day}{24\ hours} \right)}$$

Dermal Contact with soil

$$SL_{res-sol-ca-der} = \frac{TR \times AT_{Carc} \times 365\, d/yr}{\frac{SF_o}{GIABS} \times EF_r \times DFS_{adj} \times ABS_d \times 1\text{E}{-6}\, kg/mg}$$

where

$$DFS_{adj} = \left[\frac{ED_c \times SAS_c \times AF_c}{BW_c} + \frac{ED_a \times SAS_a \times AF_a}{BW_a} \right]$$

Total

$$C_{res-sol-ca-tot} = \frac{1}{\frac{1}{SL_{res-sol-ca-ing}} + \frac{1}{SL_{res-sol-ca-inh}} + \frac{1}{SL_{res-sol-ca-der}}}$$

Table 1: Equations Used to Develop Soil Screening Levels for the Direct Contact Pathways for a Residential Exposure Scenario

(page 2 of 3)

Noncarcinogenic (Hazard) – Residential

Incidental ingestion of soil

$$C_{res\text{-}sol\text{-}nc\text{-}ing} = \frac{THQ \times BW_c \times AT_{nc} \times ED_c \times 365\,d/yr}{EF_r \times ED_c \times \frac{1}{RfD_o} \times IRS_c \times \frac{1E-6kg}{mg}}$$

Inhalation of particulates and volatiles

$$C_{res\text{-}sol\text{-}nc\text{-}inh} = \frac{THQ \times AT_{nc} \times ED_c \times 365\,d/yr}{EF_r \times ED_c \times ET_r \times \frac{1\,day}{24\,hours} \times \frac{1}{RfC}\left(VF_r + \frac{1}{PEF_r}\right)}$$

Dermal contact with soil

$$C_{res\text{-}sol\text{-}nc\text{-}der} = \frac{THQ \times BW_c \times AT_{nc} \times ED_c \times 365\,d/yr}{EF_r \times ED_c \times \frac{1}{(RfD_o \times GIABS)} \times SAS_c \times AF_c \times ABS_d \times \frac{1E-6\,kg}{mg}}$$

Total

$$C_{res-sol-nc-tot} = \frac{1}{\frac{1}{SL_{res-sol-nc-ing}} + \frac{1}{SL_{res-sol-nc-inh}} + \frac{1}{SL_{res-sol-nc-der}}}$$

Table 1: Equations Used to Develop Soil Screening Levels for the Direct Contact Pathways for a Residential Exposure Scenario

(page 3 of 3)

Carcinogenic – Mutagenic

Incidental ingestion of soil

$$SL_{res-sol-mu-ing} = \frac{TR \times AT_{Carc} \times 365 d/yr}{SF_o \times EF_r \times IFSM_{adj} \times 1\text{E}-6\, kg/mg}$$

where

$$IFSM_{adj} = \frac{ED_{0\text{-}2}(2years) \times IRS_c \times 10}{BW_c} + \frac{ED_{2\text{-}6}(4years) \times IRS_c \times 3}{BW_c} + \frac{ED_{6\text{-}16}(10years) \times IRS_a \times 3}{BW_a} + \frac{ED_{16\text{-}30}(14years) \times IRS_a \times 1}{BW_a}$$

Inhalation of particulates and volatiles

$$SL_{res-sol-mu-inh} = \frac{TR \times AT_{Carc} \times 365 d/yr}{IUR \times \left(\frac{1000\,\mu g}{mg}\right) \times EF_r \times \left(VF_{s\_r} + \frac{1}{PEF_r}\right) \times ET_r \times \left(\frac{1\ day}{24\ hours}\right) \times \left(\begin{array}{l} ED_{0-2}(2years) \times 10 + ED_{2-6}(4years) \times 3 + \\ ED_{6-16}(10years) \times 3 + ED_{16-30}(14years) \times 1 \end{array}\right)}$$

Dermal Contact with soil

$$SL_{res-sol-mu-der} = \frac{TR \times AT_{Carc} \times 365 d/yr}{\frac{SF_o}{GIABS} \times EF_r \times DFSM_{adj} \times ABS_d \times 1\text{E}-6\, kg/mg}$$

where

$$DFSM_{adj} = \left[\begin{array}{l} \frac{ED_{0\text{-}2}(2years) \times SAS_c \times AF_c \times 10}{BW_c} + \frac{ED_{2\text{-}6}(4years) \times SAS_c \times AF_c \times 3}{BW_c} + \\ \frac{ED_{6\text{-}16}(10years) \times SAS_a \times AF_a \times 3}{BW_a} + \frac{ED_{16\text{-}30}(14years) \times SAS_a \times AF_a \times 1}{BW_a} \end{array}\right]$$

Total

$$C_{res-sol-mu-tot} = \frac{1}{\frac{1}{SL_{res-sol-mu-ing}} + \frac{1}{SL_{res-sol-mu-inh}} + \frac{1}{SL_{res-sol-mu-der}}}$$

Table 2: Equations Used to Develop Soil Screening Levels for the Direct Contact Pathways for a Commercial/Industrial Exposure Scenario

Carcinogenic – Commercial/Industrial (c/i)

Incidental ingestion of soil

$$SL_{c/i-sol-ca-ing}=\frac{TR\times AT_{Carc}\times 365d/yr\times BW_{c/i}}{SF_o\times EF_{c/i}\times ED_{c/i}\times IRS_{c/i}\times 1\mathrm{E}-6\,kg/mg}$$

Inhalation of particulates and volatiles

$$SL_{c/i-sol-ca-inh}=\frac{TR\times AT_{Carc}\times 365d/yr}{IUR\times\left(\frac{1000\,\mu g}{mg}\right)\times EF_{c/i}\times\left(VF_{c/i}+\frac{1}{PEF_{c/i}}\right)\times ED_{c/i}\times ET_{c/i}\times\left(\frac{1\ day}{24\ hours}\right)}$$

Dermal Contact with soil

$$SL_{c/i-sol-ca-der}=\frac{TR\times AT_{Carc}\times 365d/yr\times BW_{c/i}}{\frac{SF_o}{GIABS}\times EF_{c/i}\times ED_{c/i}\times SAS_{c/i}\times AF_{c/i}\times ABS_d\times 1\mathrm{E}-6\,kg/mg}$$

Total

$$C_{c/i-sol-ca-tot}=\frac{1}{\frac{1}{SL_{c/i-sol-ca-ing}}+\frac{1}{SL_{c/i-sol-ca-inh}}+\frac{1}{SL_{c/i-sol-ca-der}}}$$

Noncarcinogenic – Commercial/Industrial

Incidental ingestion of soil

$$C_{c/i\text{-}sol\text{-}nc\text{-}ing}=\frac{THQ\times BW_{c/i}\times AT_{nc}\times ED_{c/i}\times 365d/yr}{EF_{c/i}\times ED_{c/i}\times\frac{1}{RfD_o}\times IRS_{c/i}\times\frac{1E-6kg}{mg}}$$

Inhalation of particulates and volatiles

$$C_{c/i\text{-}sol\text{-}nc\text{-}inh}=\frac{THQ\times AT_{nc}\times ED_{c/i}\times 365d/yr}{EF_{c/i}\times ED_{c/i}\times ET_{c/i}\times\frac{1day}{24hours}\times\frac{1}{RfC}\left(VF_{c/i}+\frac{1}{PEF_{c/i}}\right)}$$

Dermal contact with soil

$$C_{c/i\text{-}sol\text{-}nc\text{-}der}=\frac{THQ\times BW_{c/i}\times AT_{nc}\times \mathrm{ED}_{c/i}\times 365\,\mathrm{d/yr}}{EF_{c/i}\times \mathrm{ED}_{c/i}\times\frac{1}{(\mathrm{RfD_o}\times\mathrm{GIABS})}\times\mathrm{SAS}_{c/i}\times\mathrm{AF}_{c/i}\times\mathrm{ABS_d}\times\frac{1\mathrm{E}-6\mathrm{kg}}{\mathrm{mg}}}$$

Total

$$C_{c/i-sol-nc-tot}=\frac{1}{\frac{1}{SL_{c/i-sol-nc-ing}}+\frac{1}{SL_{c/i-sol-nc-inh}}+\frac{1}{SL_{c/i-sol-nc-der}}}$$

Table 3: Equations Used to Develop Soil Screening Levels for the Direct Contact Pathways for a Utility Trench Worker or Construction Exposure Scenario

Carcinogenic – Utility Trench Worker (ut)

Incidental ingestion of soil

$$SL_{ut-sol-ca-ing}=\frac{TR\times AT_{Carc}\times 365d/yr\times BW_{ut}}{SF_o\times EF_{ut}\times ED_{ut}\times IRS_{ut}\times 1\mathrm{E}-6\,kg/mg}$$

Inhalation of particulates and volatiles

$$SL_{ut-sol-ca-inh}=\frac{TR\times AT_{Carc}\times 365d/yr}{IUR\times\left(\frac{1000\,\mu g}{mg}\right)\times EF_{ut}\times\left(VF_{ut}+\frac{1}{PEF_{ut}}\right)\times ED_{ut}\times ET_{ut}\times\left(\frac{1\ day}{24\ hours}\right)}$$

Dermal Contact with soil

$$SL_{ut-sol-ca-der}=\frac{TR\times AT_{Carc}\times 365d/yr\times BW_{ut}}{\frac{SF_o}{GIABS}\times EF_{ut}\times ED_{ut}\times SAS_{ut}\times AF_{ut}\times ABS_d\times 1\mathrm{E}-6\,kg/mg}$$

Total

$$C_{ut-sol-ca-tot}=\frac{1}{\frac{1}{SL_{ut-sol-ca-ing}}+\frac{1}{SL_{ut-sol-ca-inh}}+\frac{1}{SL_{ut-sol-ca-der}}}$$

Noncarcinogenic – Utility Trench Worker

Incidental ingestion of soil

$$C_{ut\text{-}sol\text{-}nc\text{-}ing}=\frac{THQ\times BW_{ut}\times AT_{nc}\times ED_{ut}\times 365d/yr}{EF_{ut}\times ED_{ut}\times\frac{1}{RfD_o}\times IRS_{ut}\times\frac{1E-6kg}{mg}}$$

Inhalation of particulates and volatiles

$$C_{ut\text{-}sol\text{-}nc\text{-}inh}=\frac{THQ\times AT_{nc}\times ED_{ut}\times 365d/yr}{EF_{ut}\times ED_{ut}\times ET_{ut}\times\frac{1day}{24hours}\times\frac{1}{RfC}\left(VF_{ut}+\frac{1}{PEF_{ut}}\right)}$$

Dermal contact with soil

$$C_{ut\text{-}sol\text{-}nc\text{-}der}=\frac{THQ\times BW_{ut}\times AT_{nc}\times ED_{ut}\times 365d/yr}{EF_{ut}\times ED_{ut}\times\frac{1}{(RfD_o\times GIABS)}\times SAS_{ut}\times AF_{ut}\times ABS_d\times\frac{1E-6kg}{mg}}$$

Total

$$C_{ut-sol-nc-tot}=\frac{1}{\frac{1}{SL_{ut-sol-nc-ing}}+\frac{1}{SL_{ut-sol-nc-inh}}+\frac{1}{SL_{ut-sol-nc-der}}}$$

Table 4: Default Exposure Parameters (continued)

Parameter	Variable Name	Units	Value	Reference
Averaging time for carcinogens	AT_{carc}	days	365 x 70	70 years by definition (USEPA 1989)
Averaging time for noncarcinogens	AT_{nc}	days	365 x ED	USEPA 1989
Body weight, residential child	BW_c	kg	15	DTSC HERO (2011)
Body weight, residential adult	BW_a	kg	70	DTSC HERO (2011)
Body weight, commercial/industrial	$BW_{c/i}$	kg	70	DTSC HERO (2011)
Body weight, utility worker	BW_{ut}	kg	70	DTSC HERO (2011)
Exposure duration, residential child	ED_c	years	6	DTSC HERO (2011)
Exposure duration, residential adult	ED_a	years	24	DTSC HERO (2011)
Exposure duration, commercial/industrial	$ED_{c/i}$	years	25	DTSC HERO (2011)
Exposure duration, utility worker	ED_{ut}	years	1	DTSC HERO (2011)
Exposure frequency, residential	EF_r	d/year	350	DTSC HERO (2011)
Exposure frequency, commercial/industrial	$EF_{c/i}$	d/year	250	DTSC HERO (2011)
Exposure frequency, utility worker	EF_{ut}	d/year	250	DTSC HERO (2011)
Exposure time for outdoor air, residential	ET_r	hours/day	24	DTSC HERO (2011)
Exposure time for outdoor air, commercial/industrial	$ET_{c/i}$	hours/day	8	DTSC HERO (2011)
Exposure time for outdoor air, utility worker	ET_{ut}	hours/day	8	DTSC HERO (2011)
Soil ingestion rate, residential child	IRS_c	mg/d	200	DTSC HERO (2011)
Soil ingestion rate, residential adult	IRS_a	mg/d	100	DTSC HERO (2011)
Soil ingestion rate, commercial/industrial	$IRS_{c/i}$	mg/d	100	DTSC HERO (2011)
Soil ingestion rate, utility worker	IRS_{ut}	mg/d	330	DTSC HERO (2011)
Soil to skin adherence factor, residential child	AF_c	mg/cm^2	0.2	DTSC HERO (2011)
Soil to skin adherence factor, residential adult	AF_a	mg/cm^2	0.07	DTSC HERO (2011)
Soil to skin adherence factor, commercial/industrial	$AF_{c/i}$	mg/cm^2	0.2	DTSC HERO (2011)
Soil to skin adherence factor, utility worker	AF_{ut}	mg/cm^2	0.8	DTSC HERO (2011)
Skin surface area exposed to soil, residential child	SAS_c	cm^2/d	2900	DTSC HERO (2011)
Skin surface area exposed to soil, residential adult	SAS_a	cm^2/d	5700	DTSC HERO (2011)

Table 4: Default Exposure Parameters (concluded)

Parameter	Variable Name	Units	Value	Reference
Skin surface area exposed to soil, commercial/industrial	$SAS_{c/i}$	cm^2/d	5700	DTSC HERO (2011)
Skin surface area exposed to soil, utility worker	SAS_{ut}	cm^2/d	5700	DTSC HERO (2011)
Particulate emission factor, residential	PEF_r	m^3/kg	1.3×10^9	DTSC HERO (2011)
Particulate emission factor, commercial/industrial	$PEF_{c/i}$	m^3/kg	1.3×10^9	DTSC HERO (2011)
Particulate emission factor, utility worker	PEF_{ut}	m^3/kg	1.0×10^6	DTSC HERO (2011)
Dermal absorption factor from soils	ABS_d	unitless	See Table 7	
Gastrointestinal absorption factor	$GIABS$	unitless	See Table 7	
Oral cancer slope factor	SF_o	1/(mg/kg-d)	See Table 7	
Inhalation Unit Risk	IUR	$1/(ug/m^3)$	See Table 7	
Oral reference dose	RfD_o	mg/kg-d	See Table 7	
Inhalation reference dose	RfC	mg/m^3	See Table 7	
Target hazard quotient	THQ	unitless	1	OEHHA (2005)
Target individual excess lifetime cancer risk	TR	unitless	1×10^{-6}	OEHHA (2005)

References:

ASTM (1996). American Society for Testing and Materials, Standard Guide to Risk-Based Corrective Action Applied at Petroleum Release Sites, ASTM E1739-95, Philadelphia, PA.

DTSC HERO (2011). Department of Toxic Substances Control, Office of Human and Ecological Risk (HER0). Human Health Risk Assessment (HHRA) Note Number 1. Recommended DTSC Default Exposure Factors for Use in Risk Assessment at California Hazardous Waste Sites and Permitted Facilities. May 20, 2011

OEHHA (2005). Human-Exposure-Based Screening Numbers Developed to Aid Estimation of Cleanup Costs for Contaminated Soil, Integrated Risk Assessment Branch, Office of Environmental Health Hazard Assessment. (Cal/EPA).

USEPA. **1989**. Risk Assessment Guide for Superfund (RAGS) Volume I Human Health Evaluation Manual (Part A) EPA/540/1-89/002, Office of Emergency and Remedial Response. December 1989.

Table 5: Equations Used to Estimate Volatilization and Particulate Emission Factors

Volatilization and Particulate Emission Factors

Effective Diffusion Coefficient (D_{eff})

$$D_{eff} = D_{air}\left(\frac{\theta_a^{10/3}}{\theta_T^{2}}\right) + D_{water}\,\frac{1}{H}\left(\frac{\theta_W^{10/3}}{\theta_T^{2}}\right)$$

Volatilization Factor (VF)

Infinite source:

$$\mathrm{VF}\left[\frac{(\mathrm{mg/m^3-air})}{(\mathrm{mg/kg-soil})}\right] = \frac{2\cdot \mathrm{W}\cdot \rho_b}{\mathrm{U_{air}}\cdot \delta_{air}}\sqrt{\frac{\mathrm{D_{eff}}\cdot \mathrm{H}}{\pi(\theta_w + \mathrm{FOC}\cdot \mathrm{K_{oc}}\cdot \rho_b + \mathrm{H}\cdot \theta_a)\mathrm{tau}}} \times 10^3\ \frac{\mathrm{cm^3kg}}{\mathrm{m^3g}}$$

Mass-balance considered:

$$VF\left[\frac{(mg/m^3-air)}{(mg/kg-soil)}\right] = \frac{W\cdot \rho_b\cdot d}{U_{air}\cdot \delta_{air}\cdot tau}\times 10^3\ \frac{cm^3kg}{m^3g}$$

Calculate VF using both equations, then use the lower of the two values.

VF_r : Use tau = $tau_c + tau_r$

$VF_{c/i}$: Use tau = $tau_{c/i}$

VF_{ut} : Use tau = tau_{ut}

Table 6: Default Volatilization and Soil-Specific Parameters

Parameter	Variable Name	Units	Value	Reference
Fraction organic carbon in soil	FOC	g OC/g soil	0.01	ASTM (1996)
Thickness of impacted soil	d	cm	305	ASTM (1996) (10 feet)
Wind speed in outdoor air mixing zone	U_{air}	cm/s	225	ASTM (1996)
Width of source area parallel to wind, or groundwater flow direction	W	cm	2500	ASTM (1996)
Outdoor air mixing zone height	δ_{air}	cm	200	ASTM (1996)
Volumetric air content in vadose-zone soils	Θ_A	(cm^3 air)/(cm^3 soil)	0.26	ASTM (1996)
Total soil porosity	θ_T	(cm^3 voids)/(cm^3 soil)	0.38	ASTM (1996)
Volumetric water content in vadose-zone soils	Θ_W	(cm^3 water)/(cm^3 soil)	0.12	ASTM (1996)
Soil bulk density	ρ_b	g/cm^3	1.7	ASTM (1996)
Averaging time for vapor flux, residential adult	tau_r	s	7.57E8	ASTM (1996) = ED_r in sec
Averaging time for vapor flux, residential child	tau_c	s	1.89E8	ASTM (1996) = ED_c in sec
Averaging time for vapor flux, commercial/industrial	$tau_{c/i}$	s	7.88E8	ASTM (1996) = $ED_{c/i}$ in sec
Averaging time for vapor flux, utility worker	tau_{ut}	s	3.15E7	ASTM (1996) = ED_{ut} in sec
Effective diffusion coefficient in soil	D_{eff}	cm^2/s	Chem. specific	calculated
Diffusion coefficient in air	D_{air}	cm^2/s	Chem. specific	See Table 7.
Diffusion coefficient in water	D_{water}	cm^2/s	Chem. specific	See Table 7.
Organic carbon-water sorption coefficient	K_{oc}	mL/g	Chem. specific	See Table 7.
Henry's Law coefficient	H	(cm^3 water)/(cm^3 air)	Chem. specific	See Table 7.

References:

ASTM. 1996. Standard Guide to Risk-Based Corrective Action Applied at Petroleum Release Sites, ASTM E1739-95, Philadelphia, PA.

Table 7: Chemical Parameter Values

Chemical Parameters	**Units**	**Benzene**	**Ethyl-benzene**	**Naphtha-lene**	**PAH**[1]	**Reference**
Henry's Law constant	-	0.23	0.32	0.02	2.0E-5	SF RWQCB ESLs
Organic carbon partition coefficient	ml/g	58.9	360	1200	5.5E+6	SF RWQCB ESLs
Diffusion coefficient in air	cm^2/s	0.088	0.075	0.059	ND	SF RWQCB ESLs
Diffusion coefficient in water	cm^2/s	9.8E-6	7.8E-6	7.5E-6	ND	SF RWQCB ESLs
Toxicity Parameters						
Oral slope factor (SF_o)	1/(mg/kg-d)	0.1	0.011	ND	1.7	OEHHA (2009, 2010 – BaP PHG)
Inhalation unit risk (IUR)	$1/(\mu g/m^3)$	2.9E-5	2.5E-6	3.4E-5	1.1E-3	OEHHA (2009)
Oral reference dose (RfD_o)	mg/kg-d	0.004	0.1	0.020	ND	USEPA IRIS
Reference concentration (RfC)	mg/m^3	0.060	2	0.009	ND	OEHHA RELs
Dermal absorption factor from soil	-	ND	ND	0.13	0.13	SF RWQCB ESLs
Gastrointestinal absorption factor	-	1	1	1	1	SF RWQCB ESLs

ND = No Data

SF RWQCB ESLs. Regional Water Quality Control Board (RWQCB) Region 2 – San Francisco. 2008. Screening for Environmental Concerns at Sites with Contaminated Soil and Groundwater. Interim Final. May

OEHHA (2009). OEHHA Cancer Potency Values as of July 21, 2009.

OEHHA RELs. OEHHA Chronic Reference Exposure Levels (RELs). http://www.oehha.ca.gov/risk/chemicaldb/

USEPA IRIS. USEPA Integrated Risk Information System on-line database.

[1] The chemical properties for benzo(a)pyrene were used as a surrogate for the "PAH" group.

Table 8: Soil Screening Levels for Each Receptor

Chemical	Residential		Commercial/ Industrial		Utility Worker
	0 to 5 feet bgs mg/kg	Volatilization to outdoor air (5 to 10 feet bgs) mg/kg	0 to 5 feet bgs mg/kg	Volatilization to outdoor air (5 to 10 feet bgs) mg/kg	0 to 10 feet bgs mg/kg
Benzene	1.9	2.8	8.2	12	14
Ethylbenzene	21	32	89	134	314
Naphthalene	9.7	9.7	45	45	219
PAH*	0.063**	NA	0.68	NA	4.5

* Based on the seven carcinogenic PAHs as benzo(a)pyrene toxicity equivalent [BaPe]. The PAH screening level is only applicable where soil is affected by either waste oil and/or Bunker C fuel.

** DTSC (2009) reports average ambient PAH concentrations (as BaPe) in California ranging from 0.16 to 0.21 mg/kg, and upper tolerance limits (UTLs) ranging from 0.9 to 1.5 mg/kg. The screening level shown in this table is "risk-based" and therefore in this case is far below the average ambient concentrations for PAHs in California. It is suggested that DTSC (2009) be consulted for sites with PAH contamination.

NA = Not Applicable

FIGURES

Figure 1. Conceptual Site Model for the Soil Screening Levels.

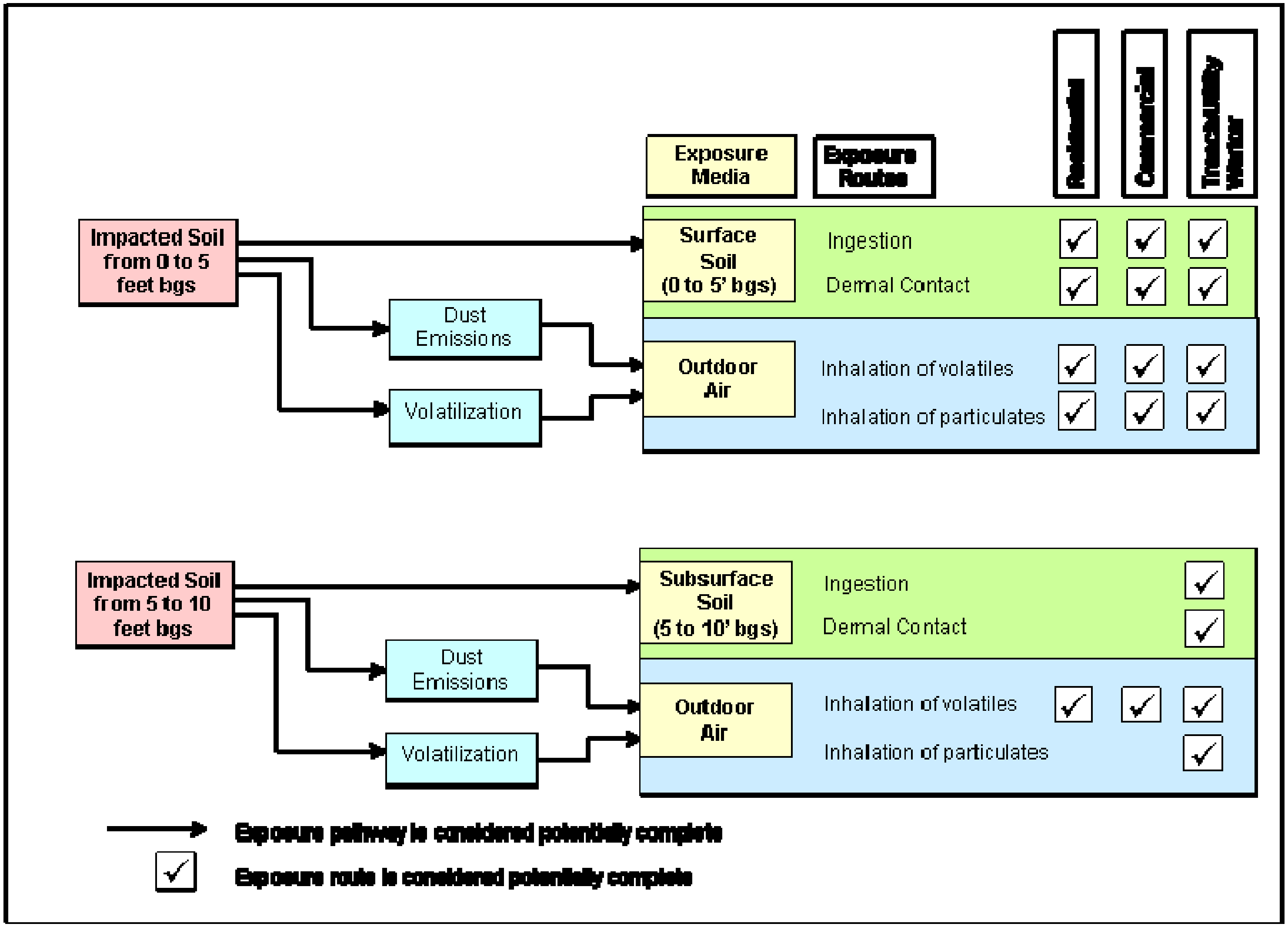
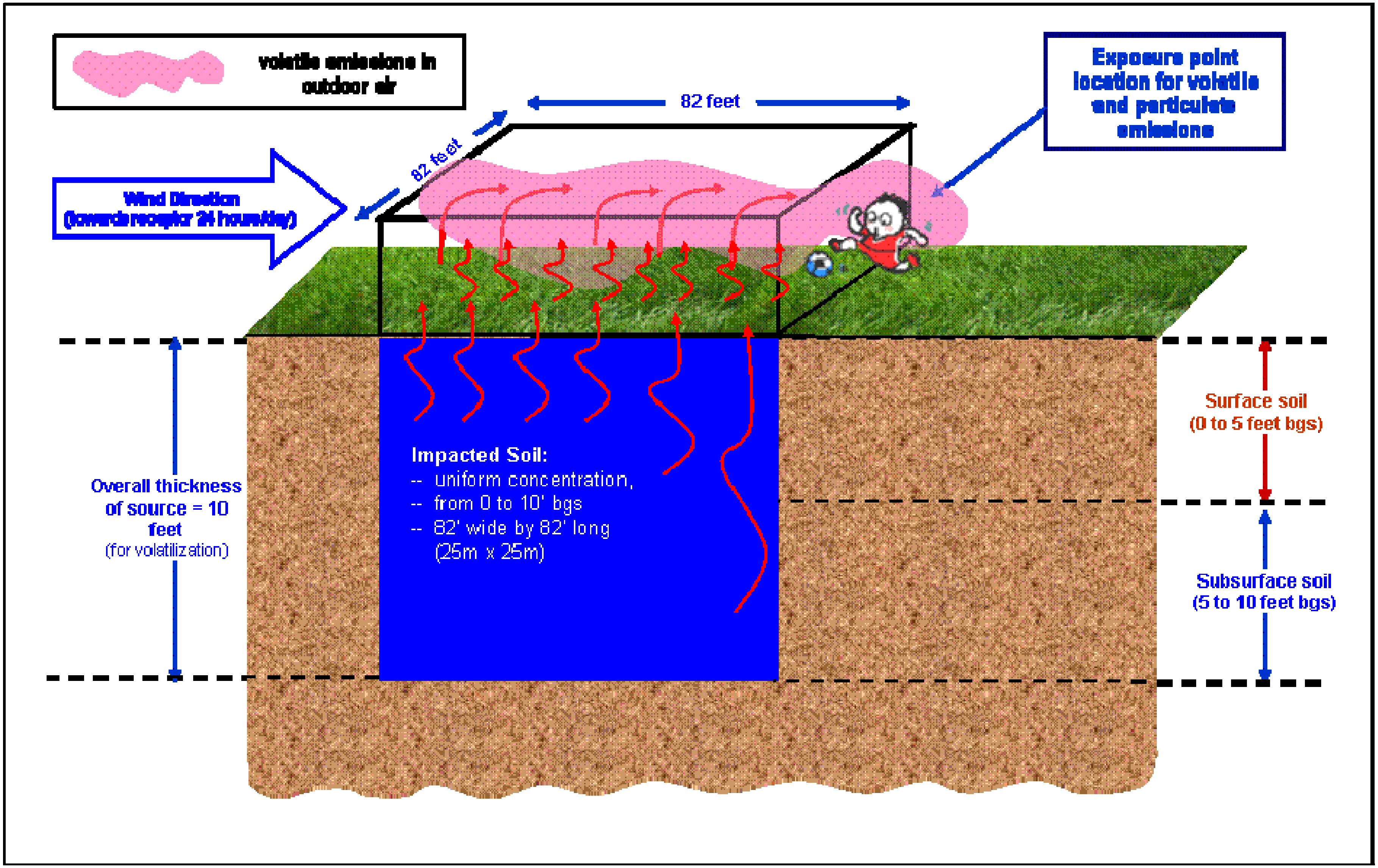


Figure 2. Schematic for the ASTM Volatilization Factor.



Technical Justification for Groundwater Media-Specific Criteria

(Final 04-24-2012)

1 INTRODUCTION

The purpose of this document is to supplement and provide technical justification for groundwater media-specific criteria described in the General Criteria and Media Specific Criteria sections of the Low-Threat Underground Storage Tank (UST) Case Closure Policy (Policy). Media-specific criteria for vapor and soil are discussed in the documents *Technical Justification for Vapor Intrusion Media-Specific Criteria,* and *Technical Justification for Soil Screening Levels for Direct Contact and Outdoor Air Exposure Pathways,* respectively.

2 BACKGROUND

The background section presents information on petroleum chemistry, free product, plume studies, and the use of Conceptual Site Models (CSMs).

2.1 Petroleum Chemistry

Petroleum is defined as crude oil, or any fraction thereof, which is liquid at standard conditions of temperature and pressure, which means 60 degrees Fahrenheit and 14.7 pounds per square inch absolute. Petroleum enters the subsurface as an immiscible fluid which is a mixture of constituents. These petroleum constituents are unique in the subsurface and their fate is predictable.

The composition of the dissolved phase from unweathered petroleum products (including gasoline, kerosene, jet fuel, diesel, Bunker C fuel, and motor oil) and unweathered crude oils have been studied and investigated under laboratory conditions by several researchers using various analytical methods (Coleman, et al. 1984; Shi, et. Al. 1990; Thomas and Delfino 1991; Bruya and Friedman 1992; Chen, et al. 1994; and Potter 1996). The results from these studies are consistent, and provide clear evidence that the petroleum hydrocarbons, which comprise the measurable dissolved phase of unweathered crude oil and refined products, are limited primarily to these discrete constituents:

- Six to eleven carbon atoms (C^6 to C^{11}) monoaromatics (benzene, toluene, ethylbenzene, and xylenes [BTEX] and the alkylated benzenes);
- C^{10} to C^{14} polyaromatic hydrocarbons (PAHs) (naphthalene, alkylated naphthalenes, acenaphthene, fluorene, phenanthrene, and anthracene); and
- C^6 and smaller aliphatics.

These studies focused on the hydrocarbon constituents of unweathered crude oil and refined products in the dissolved phase; however, the same principles apply to weathered products. Blending agents or additives which are polar in their molecular structure, such as oxygenates, have both relatively high pure-compound solubilities and large mole-fractions within the product mixture; therefore, they can represent a large proportion of the dissolved phase of a given product. This is why methyl tertiary butyl ether (MTBE) is present in plumes in much higher concentrations than the hydrocarbons. Note that polar molecules have slightly charged negative and positive ends, and therefore are more soluble in water, which is also polar.

The scientific community has known for more than 15 years that the vast majority of risk posed to human health and water quality is driven by the aromatics within the BTEX suite (benzene in particular) and the oxygenate MTBE. The BTEX compounds have relatively high toxicity and are the hydrocarbon constituents with the highest effective solubility in gasoline. MTBE has very high effective solubility, has relatively low biodegradation potential, and therefore creates longer plumes. MTBE has lower toxicity than benzene, but it has a low taste and odor threshold, therefore its California Maximum Contaminant Level (MCL) is low as well. While the rest of the hydrocarbons make up the majority of the mass in the product that may be present, they account for very little risk posed to human health or groundwater quality due to their lower toxicity and/or lower mobility in the environment.

2.2 Free Product

Free product or light non-aqueous phase liquid (LNAPL) exists in three conditions in the subsurface: 1) residual or immobile LNAPL (LNAPL that is trapped in the soil pore spaces by capillary forces and is not mobile), 2) mobile LNAPL (enough LNAPL is present in the soil pore spaces to overcome capillary forces so that the LNAPL can move), and 3) migrating LNAPL (mobile LNAPL that is migrating because of a driving head). Residual, mobile, and migrating LNAPL are described in detail in several peer-reviewed technical documents, including the 2009 Interstate Technology Regulatory Council (ITRC) Technical/Regulatory Guidance *Evaluating LNAPL Remedial Technologies for Achieving Project Goals*. (ITRC, 2009)

The term free product is primarily equivalent to migrating LNAPL (a subset of mobile LNAPL), and secondarily equivalent to mobile LNAPL. Whether LNAPL is mobile (and therefore could potentially migrate) or not is usually tested by observing recharge of LNAPL after removing LNAPL from a monitoring well. Whether LNAPL is migrating or not is tested by monitoring the extent of the LNAPL body (usually using the apparent product thickness in monitoring wells) at a certain water level elevation over time. If the extent at that water level elevation does not expand, then the LNAPL is not migrating. Therefore, LNAPL must be removed to the point that its migration is stopped, and the LNAPL extent is stable. Further removal of LNAPL is required to the extent practicable at the discretion of the local agency.

Removal of LNAPL from the subsurface is technically complicated, and removal of LNAPL to the maximum extent practicable is based on site-specific factors (such as soil properties, varying groundwater elevations, and varying lateral groundwater flow velocities) and includes a combination of objectives for the LNAPL removal (such as whether the LNAPL is a significant source of dissolved constituents to groundwater or volatile constituents to soil vapor, or whether there is a high likelihood that hydrogeologic conditions would change significantly in the future which may allow the mobile LNAPL to migrate) and technical limitations. The typical objectives for LNAPL removal, technologies for

LNAPL removal and technical limitations of LNAPL removal are discussed in several peer-reviewed technical documents within ITRC (2009).

Studies in California show that once the contaminant source is removed and the plume stabilizes, natural degradation proceeds at substantial rates, sometimes at 50-60% per year (Rice et. al., 1995). Therefore, if free product is removed to the maximum extent practicable and natural degradation is occurring, then it is reasonable to expect that attenuation would continue.

2.3 Plume Studies

Plume length studies recognize that petroleum plumes stabilize in length due to natural attenuation. Various researchers have conducted multi-site studies of groundwater plume lengths at petroleum release sites across the United States. These studies considered sites where active remediation was performed and sites where no active remediation was performed. Many studies focused on benzene plumes (Rice, et al. 1995; Rice et al. 1997; Busheck et al. 1996; Mace, et al. 1997; Groundwater Services, Inc. 1997; American Petroleum Institute (API) 1998); other researchers (Dahlen et al. 2004; Shih et al. 2004) studied both benzene and oxygenate plumes, including MTBE. Many of the researchers recognized benzene, MTBE, and total petroleum hydrocarbons as gasoline (TPHg) as key indicator constituents for groundwater plume lengths. Researchers' technical justification for using these three constituents as key indicators relied on the facts that: 1) benzene has the greatest toxicity of the soluble petroleum constituents, 2) MTBE typically has the greatest plume lengths, and 3) TPHg represents the additional dissolved hydrocarbons that may be present resulting from a typical petroleum release. The peer-reviewed study of plume lengths at 500 petroleum UST sites in the Los Angeles area is widely accepted as representative of plume lengths at California UST sites (Shih et. al., 2004). Shih et. al. (2004) reports benzene, MTBE and TPHg plume characteristics as follows:

Table 1: Plume characteristics reported by Shih et. al. (2004).

Constituent (and plume limit concentration)	Average Plume Length (feet)	90th Percentile Plume Length (feet)	Maximum Plume Length (feet)
Benzene (5 µg/l)	198	350	554
MTBE (5 µg/l)	317	545	1,046
TPHg (100 µg/l)	248	413	855

Notes:

1. Plume lengths were measured from the source area.
2. Total petroleum hydrocarbons as gasoline (TPHg) is shown for comparison purposes only. The Policy does not set criteria for TPH.
3. Constituent concentrations measured in micrograms per liter (µg/l).

Although the California maximum contaminant level for benzene is 1 micrograms per liter (µg/l), the Shih et al. (2004) study used a benzene concentration of 5 µg/l to determine plume length because of the statistical uncertainty associated with concentrations near the 0.5 µg/l laboratory reporting limit. Benzene plume lengths measured at a 1.0 µg/l concentration limit could be expected to be slightly longer than those tabulated above.

Ruiz-Aguilar et al. (2003) studied releases of ethanol-amended gasoline (10% ethanol by volume) at UST release sites in the Midwest. Ruiz-Aguilar et al. (2003) found that benzene plume lengths may increase by 40% to 70% when gasoline is formulated with 10% ethanol substituted for MTBE. Ethanol preferentially biodegrades prior to benzene, which results in a longer benzene plume.

Natural attenuation of petroleum hydrocarbon and oxygenate plumes has been documented by many researchers since the 1990s. This body of work demonstrates that natural attenuation of petroleum hydrocarbons and MTBE occurs under both aerobic and anaerobic conditions (Howard, 1990). Advances in compound-specific stable isotope analyses make it possible to accurately measure the shift in the ratio of the isotopes in MTBE in water at low concentrations. The fractionation of the MTBE that has not degraded becomes the equivalent to a metabolic product that is used to document biodegradation. This makes it possible for the first time to unequivocally identify and measure anaerobic biodegradation of MTBE at field scale (U.S. EPA, 2005). The rate of degradation/attenuation depends on the constituent and the plume bio/geochemical conditions.

2.4 Conceptual Site Model

A CSM is used to identify contaminant source(s), transport mechanisms or exposure pathways, and potential receptors based on site-specific and regional conditions. It provides a conceptual understanding of contaminant transport and risk assessment at a site. The CSM is a fundamental element of a comprehensive site investigation and contains sufficient detail to make decisions at the site, and comprehensive enough to show compliance with all of the policy media-specific criteria and State and federal laws and/or regulations. The CSM is an iterative thought process that is always implemented at a leaking underground fuel tank (LUFT) site, whether or not it is recorded as a tangible document, graphic, or depiction. To discuss and make decisions about LUFT sites, one must visualize the source and the movement of contaminants in the subsurface and create a model or analogy. Although the term conceptual site model is not found in California law or regulations, the thought process is fundamental to scientific inquiry and is directly applicable to decision-making at LUFT sites.

The objectives of the CSM are:

- To convey an understanding of the origin, nature, and lateral and vertical extent of contamination;
- To identify potential contaminant fate-and-transport processes and pathways. This includes but is not limited to identifying the site topography, regional and site-specific geologic and hydrologic conditions, designated beneficial uses of groundwater beneath the site, and plume stability;
- To identify potential human and environmental receptors that may be impacted by contamination associated with the site;
- To guide site investigation activities and identify additional data needed (if any) to draw reasonable conclusions regarding the source(s), pathways, and receptors; and
- To evaluate risk to human health, safety, and the environment posed by releases at a LUFT site.

3 GENERAL CRITERIA

The Policy indicates the following general criteria must be satisfied by all candidate sites:

a. The unauthorized release is located within the service area of a public water system;

b. The unauthorized release consists only of petroleum;

c. The unauthorized (primary) release from the UST system has been stopped;

d. Free product has been removed to the maximum extent practicable;

e. A conceptual site model that assesses the nature, extent, and mobility of the release has been developed;

f. Secondary source has been removed to the extent practicable;

g. Soil or groundwater has been tested for MTBE and results reported in accordance with Health and Safety (Health & Saf.) Code § 25296.15; and

h. Nuisance as defined by Wat. Code § 13050 does not exist at the site.

This section focuses on providing technical justification for the general criteria that pertain to groundwater.

3.1 Public Water Systems

The Policy requires that a low-risk site be located within the service area of a public water system for low-threat site closure. The Policy limits low-threat sites to areas with available public water systems to reduce the likelihood that new wells in developing areas will be inadvertently impacted by residual petroleum in groundwater. The Policy defines a public water system as a system for the provision of water for human consumption through pipes or other constructed conveyances that has 15 or more service connections or regularly serves at least 25 individuals daily at least 60 days out of the year.

Existing programs through the California Department of Water Resources (DWR) and California Department of Public Health (CDPH) provide protective measures to limit new water supply locations in areas with potential poor water quality. DWR's Bulletin 74-81, *Water Well Standards: State of California* (1981), provides guidance on installing new wells to limit poor water quality intrusion. Additionally, CDPH implements their Drinking Water Source Assessment Program (DHS, 2000), which requires an inventory of possible contaminating activities within source areas and protection zones prior to use of a new supply well.

Water suppliers understand the groundwater basins used for water supply. Municipal wells tend to preclude shallow impacts by using deep screens and good surface sanitary seals. Municipal wells have significant dilution due to large pumping volumes. Public water systems have a greater opportunity for blending supplies in the unlikely event a new well captures and old plume. Additionally, residences in a public water system are unlikely to have a private domestic well that could be impacted by a low-threat site. It is unlikely that shallow domestic wells will be installed where a reliable source of water already exists.

Sites within a public water system that have potential to impact the water supply within a public water system would be considered high-risk and would not qualify as a low-threat site. If a water supplier determines that a site that is being considered for closure under the low-threat scenario is likely to impact future water supplies, the site may have unique conditions that could require additional remediation.

3.2 Release Consists only of Petroleum

The Policy requires that the unauthorized release consists only of petroleum for consideration as a low-threat site. While recalcitrant contaminants may require specific conditions to degrade, petroleum hydrocarbons and MTBE have shown to undergo biodegradation/natural attenuation under both aerobic and anaerobic conditions (Howard, 1990). Other non-petroleum contaminants may have different chemical properties and risks to consider and are therefore beyond the scope of the Policy.

3.3 Primary Release has been Stopped

The Policy requires that the tank, pipe, or other appurtenant structure that released petroleum into the environment has been removed, repaired or replaced for consideration as a low-threat site. This is to prevent the ongoing release of petroleum contamination from continuing in the future. If the mechanism for the primary release is not removed, repaired, or replaced, the petroleum-impacted groundwater plume is unlikely to remain stable or decrease with time and would not qualify as being a low-risk site.

3.4 Free Product Removal

The Policy requires that free product be removed to the maximum extent practicable in order to be considered a low-risk site. Free product is the primary source of contamination from LUFT sites which contributes to secondary sources and groundwater contamination. The Policy is consistent with California Code of Regulations (CCR), Title 23, Division 3, Chapter 16, §2655 et seq. that free product is required to be removed to the maximum extent practicable, and the abatement of migration shall be the predominant objective in the design of the free product removal system. Free product shall be removed in a manner that minimizes the spread of contamination into previously uncontaminated zones. For most sites, stable or declining concentrations of dissolved constituents in groundwater indicate that petroleum is no longer acting as a significant source. Therefore, removing the primary source of contamination limits the development of a secondary source (e.g., soil and groundwater). Rice et. al. (1995) has shown that if the source is removed and groundwater is stable, this can promote natural degradation and expedites compliance with the Water Quality Objectives (WQOs).

3.5 Conceptual Site Model

The Policy requires that a CSM assess the nature, extent, and mobility of the release has been developed in order to be considered a low-risk site. The CSM is a tool that uses current and historical information to evaluate whether a site is currently low-risk site and likely to remain a low-risk site in the future. It describes the dynamics of a system and is used to assess risk based on data from the site and from nearby properties. It captures current and historical surrounding property-use that impact or may impact contaminant transport at a site. It also provides a method for predicting conditions which can affect the nature, extent, and mobility of the contamination (such as soil properties, varying groundwater elevations, and varying lateral groundwater flow velocities).

3.6 Secondary Source Removal

A secondary source is defined as petroleum-impacted soil or groundwater located at or immediately beneath the point of release from the primary source. The Policy requires that the secondary source be removed to the maximum extent practicable. To the maximum extent practicable means implementing a cost-effective corrective action which removes or destroys-in-place the most readily recoverable fraction of source-area mass as determined by the implementing agency. In some cases, site attributes prevent the removal of groundwater contamination (e.g. physical or infrastructural constraints exist where removal or relocation would be technically or economically infeasible). This may result in residual concentrations to remain in groundwater above the WQOs.

Rice et al. (1995) shows that soil microorganisms severely limit the movement of plumes by digesting the balance of the petroleum-based contaminant. Data from a number of counties in California show that contaminant plumes rarely exceed 250 feet and stabilize quickly. Once contaminant sources are removed and plumes stabilize, natural degradation proceeds at substantial rates, sometimes at 50-60% per year (Rice et al., 1995). Allowing the residual contamination to remain after the secondary source removal is performed generally results in a ten-fold reduction in plume contaminant mass within one to three years.

3.7 Testing for MTBE

The Policy requires that soil and groundwater have been tested for MTBE and results reported in accordance with Health & Saf. Code §25296.15. MTBE is recognized as one of the indicator constituents for most petroleum-impacted groundwater plumes and typically has the greatest plume lengths. For these reasons, MTBE is a good indicator of plume characteristics and is useful for evaluating historical trends and refining the CSM.

3.8 Nuisance

As part of the general criteria for the Policy, a site must remediate all nuisances per Wat. Code §13050 to be considered for closure under the low-threat scenario. There can be a scenario where remaining contamination in groundwater is not a risk to human health or the environment but is a nuisance (e.g., dewatering in basement at adjoining property). This requirement would eliminate sites from being considered low-risk where there is a current or future potential that a nuisance condition exists.

Wat. Code §13050 defines nuisance as anything which meets all of the following requirements:

- Is injurious to health, or is indecent or offensive to the senses, or an obstruction to the free use of property, so as to interfere with the comfortable enjoyment of life or property;
- Affects at the same time an entire community or neighborhood, or any considerable number of persons, although the extent of the annoyance or damage inflicted upon individuals may be unequal; and
- Occurs during, or as a result of, the treatment or disposal of wastes.

The petroleum vapor intrusion and direct contact and outdoor air exposure pathways criteria listed in the Policy (and related Technical Justification documents) outline the conditions that the site must satisfy for protection of public health and for immediate unrestricted use of the property. If all general criteria are satisfied for the site, it is unlikely that the shallow groundwater will be used before water quality objectives are restored by natural attenuation.

In the unlikely event that shallow groundwater becomes a nuisance through construction dewatering, basement sump dewatering, or other activities where the shallow groundwater is contacted but not consumed, the Policy provides for abatement of nuisance conditions.

4 MEDIA-SPECIFIC CRITERIA FOR GROUNDWATER

This criteria is used to determine that threats to existing and anticipated beneficial uses of groundwater have been mitigated or are de minimus. State Water Board Resolution 92-49, *Policies and Procedures for Investigation and Cleanup and Abatement of Discharges under Water Code § 13304,* directs that water affected by an unauthorized release attain either background water quality or the best water quality that is reasonable if background water quality cannot be restored. Any alternative level of water quality less stringent than background must be consistent with the maximum benefit to the people of the State, not unreasonably affect current and anticipated beneficial use of affected water, and not result in water quality less than that prescribed in the regional water quality control plan (Basin Plan) for the basin within which the site is located. The following illustrates the method and rationale for a low-threat facility to comply with State Water Board Resolution 92-49.

4.1 Low-Threat Groundwater Justification

In general, the Low-Threat Groundwater Classes are classified on stable or decreasing plumes, status of free product removal, distance to the nearest groundwater or surface water receptor from the plume boundary, and other factors that may be required to demonstrate low-threat. Of importance, a factor of safety is applied to each class for separation distances to potential groundwater and surface water receptors. It should be noted that these groundwater plume class criteria (concentrations, plume lengths and separation distances) are only one component of the overall evaluation of site conditions that must be satisfied to be considered for closure as a low-threat site under the Policy.

For the purpose of this Policy, the length of a plume is the maximum extent from the point of release of any petroleum related constituent in groundwater that exceeds the WQOs. The plume boundary is where the constituent(s) furthest from the point of release concentration level equals the WQOs.

A plume is considered stable or decreasing if a contaminant mass has expanded to its maximum extent: the distance from the release where attenuation exceeds migration. There are two common ways to demonstrate plume stability. The first common way is to routinely observe non-detect values for groundwater parameters in down-gradient wells. The second common way is to show stable or decreasing concentration levels in down-gradient wells at the distal end of the plume. It should be noted that concentration levels may exhibit fluctuations due to seasonal variations. These variations may be also attributed to man-made factors, including but not limited to: varying sampling techniques, false positive results, or laboratory inconsistencies.

Based on the plume studies presented in the above sections, a total separation distance from the source area to the receptor of about 500 feet should be protective for 90% of plumes from UST sites, and a total separation distance from the source area to the receptor of about 1,000 feet should be protective for virtually all plumes from UST sites. Additionally, low-threat classes require a known maximum stabilized plume length, and meet all of the additional characteristics of one of the five classes of sites. Requiring that a plume must be stable or decreasing reduces uncertainty as to how long the plume might become in the future. The Policy addresses the potential for longer plumes of ethanol-enhanced gasoline by applying separation distance safety factors of 100% to 400%.

The use of separation distances is consistent with other State and local practices regarding impacts to groundwater caused by other anthropogenic releases. For example, State and local agencies establish required separation distances or setbacks between water supply wells and septic system leach fields (typically 100 feet), and sanitary sewers (typically 50 feet; [DWR 1981]).

In order to accommodate varying plume sizes, remaining free product, higher constituent concentrations, and distances to surface water and groundwater receptors, factors of safety are incorporated into low-threat groundwater classes explained in the following sections. As the associated risk increases, so does the margin of error, thus the factor of safety also increases progressively between 100 and 400 percent (%).

4.2 Low-Threat Groundwater Classes Defined

The following paragraphs present and discuss the key rationales for low-threat plume lengths, maximum concentrations, and separation distances for each low-threat class as discussed in the Policy. Note that the specified concentrations are maximums, and typically occur in source area monitoring wells; the average concentrations in the plume would be lower. These groundwater plume class criteria (concentrations, plume lengths and separation distances) are only one component of the overall evaluation of site conditions that must be satisfied to be considered for closure as a low-threat site under the Policy.

<u>Class 1:</u> The short, stabilized plume length less than 100 feet (plume boundary is less than [<] 100 feet from point of release) is indicative of a small or depleted source and/or very high natural attenuation rate. The plume boundary must be greater than 250 feet distance to a receptor. This represents an additional 250% plume length safety factor in the event that some additional unanticipated plume migration is to occur.

Class 2: The moderate, stabilized plume length (plume boundary is <250 feet from point of release) approximates the average benzene plume length from the cited studies. The maximum concentrations of benzene (3,000 µg/l) and MTBE (1,000 µg/l) in groundwater are conservative indicators that free product is not present. These concentrations are approximately 10% and 0.02%, respectively, of the typical effective solubility of benzene and MTBE in unweathered gasoline. The plume boundary must be greater than 1,000 feet distance to a receptor. This represents an additional 400% plume length safety factor in the event that some additional unanticipated plume migration is to occur. Also note that Health & Saf. Code §25292.5 requires that UST owners and operators implement enhanced leak detection for all USTs within 1,000 feet of a drinking water well. In establishing the 1,000 feet separation requirement the legislature acknowledged that 1,000 feet was a sufficient distance to establish a protective setback between operating petroleum USTs and drinking water wells in the event of an unauthorized release.

Class 3: The moderate, stabilized plume length (plume boundary is <250 feet from point of release) approximates the average benzene plume length from the cited studies. The on-site free product and/or high dissolved concentrations in the plume remaining after secondary source removal to the maximum extent practicable as per the General Criteria in the Policy require that the plume has been stable or decreasing for a minimum of five years of monitoring to validate plume stability/natural attenuation (i.e., to confirm that the rate of natural attenuation exceeds the rate of LNAPL dissolution and dissolved-phase migration). The plume boundary must be greater than 1,000 feet distance to a receptor. This represents an additional 400% plume length safety factor in the event that some additional unanticipated plume migration is to occur, and is consistent with Health & Saf. Code §25292.5 as discussed above.

Class 4: The long, stabilized plume length (plume boundary is <1,000 feet from point of release) approximates the maximum MTBE plume length (Shih et al., 2004). The plume boundary must be at least 1,000 feet distance to a receptor. This is an additional 100% plume length safety factor in the event that some additional unanticipated plume migration is to occur, and is consistent with Health & Saf. Code §25292.5 as discussed above.

Class 5: Other low-threat site-specific scenarios not captured in Class 1 through 4. Should a site not fall in one of the four classes discussed above, an analysis of site specific conditions will be used to determine if the contaminant plume poses a low-threat to human health and safety and to the environment and if the water quality objectives will be achieved within a reasonable time frame.

5 DISCUSSION

This Technical Justification for Groundwater Media-Specific Criteria document should be used in conjunction with the Policy, the Direct Contact and Outdoor Air Exposure Pathways Criteria, and Vapor

Intrusion Criteria documents to determine if a site is low-threat to human health, safety and the environment.

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Technical Justification for
Vapor Intrusion Media-Specific Criteria

(Final 03-21-2012)

1 EXECUTIVE SUMMARY

For petroleum-related volatile organic compounds (VOCs), current risk-based screening levels (such as the California Human Health Screening Levels [CHHSLs]) for evaluating risk from vapor intrusion at underground storage tank (UST) sites are conservative. This conservatism is caused by not considering biodegradation in site screening which generally drives further unnecessary site evaluation. Recent models and field studies show that bioattenuation of petroleum hydrocarbons at UST sites is significant (Abreu et al., 2009; API, 2009; Davis, 2009; Lahvis, 2011). Petroleum hydrocarbon VOCs (such as, benzene, toluene, ethylbenzene and xylenes -BTEX) concentrations have been shown to attenuate by several orders of magnitude within short vertical distances (e.g., < 2-3 m) in the unsaturated zone due to biodegradation. The hydrocarbon VOC attenuation generally increases by an additional order of magnitude (or more) when transport across a building foundation to indoor air is also considered (U.S. EPA, 2008). The characteristic occurrence of rapid hydrocarbon attenuation in the unsaturated zone is amenable to a site-screening methodology for vapor intrusion based on exclusion distances. Exclusion distances are defined as VOC source-receptor (building) separation distances beyond which the risk of vapor intrusion is assumed negligible. Note the source may be located in soil and/or groundwater. Exclusion distances can be broadly defined for two types of sources: low-concentration (e.g., dissolved-phase) and high-concentration (e.g., light non-aqueous-phase liquid – LNAPL) sources which differ substantially in chemical vapor composition and are unique with respect to their vapor intrusion risk potential.

Recent modeling studies and evaluations of field (soil-gas) data from numerous UST sites and sampling locations demonstrate that biodegradation is sufficient to limit the potential for vapor intrusion at sites with "low-concentration" (dissolved-phase) hydrocarbon sources (Abreu et al., 2009; Davis, 2009; Davis, 2010; Lahvis, 2012). For example, there is less than a 5% probability that benzene concentrations in soil gas would exceed a low screening-level for vapor intrusion (30 $\mu g/m^3$) at distances of 5 ft (~2 m) or more above a dissolved-phase benzene concentration in groundwater < 1,000 µg/L. (Note, for comparison, the CHHSL for benzene in soil gas is 83 $\mu g/m^3$ for buildings on engineered fill.) Additional attenuation (i.e., a shorter exclusion distance) is predicted to occur by transport modeling for dissolved-phase sources displaced laterally from the building foundation (Abreu and Johnson, 2005). Vapor intrusion risks are thus expected to be rare to non-existent at sites with low-concentration sources.

At sites with "high concentration" hydrocarbon sources (un-weathered residual light non-aqueous phase liquid (LNAPL) in soil and/or un-weathered free-phase LNAPL on groundwater), transport modeling shows that hydrocarbon VOCs will attenuate below levels of concern in the unsaturated zone within a distance of approximately 20 ft (~7 m) of the source. The transport modeling is based on assuming reasonable approximations of source concentration and transport within the unsaturated zone (including biodegradation rate). Soil-gas data collected at numerous UST, terminal, and manufacturing sites with LNAPL sources would suggest that the model predicted attenuation above LNAPL sources is conservative. Analysis of the field data at these types of sites shows that hydrocarbon VOCs are attenuated below screening-level concentrations within 8 – 13 ft (~3 - 4 m). Biodegradation accounts for more than 1,000x additional attenuation within 5 ft vertical distances of benzene sources in soil-gas up to 10,000,000 $\mu g/m^3$. Again, the attenuation is predicted to increase further for high (e.g., LNAPL) sources displaced laterally from building foundations (i.e. the soil gas concentrations would attenuate in even shorter distances).

The purpose of this document is to provide a technical justification for the proposed low-threat vapor intrusion scenarios. The justification is based on current, state-of-the-art science on separation distances between source and receptor that are human-health protective. A few of the most recent studies cited below are awaiting publication (but are available for review). All cited studies should be considered in the development of a rational, technically defensible approach to vapor intrusion screening.

The four scenarios presented in the *Low-Threat UST Closure Policy* are:

Scenario 1: Un-weathered LNAPL on groundwater

30 ft vertical source/building separation (exclusion) distance for un-weathered (residual or free-phase) LNAPL on groundwater

Scenario 2: Un-weathered LNAPL in soil

30 ft lateral and vertical separation (exclusion) distance between a building foundation and an un-weathered LNAPL (residual or free-phase) source in soil.

Scenario 3: Dissolved phase benzene concentrations in groundwater

- 5 ft. vertical separation distance between a dissolved-phase source < 100 µg/L benzene and a building foundation (no oxygen (O_2) measurement)
- 10 ft. vertical exclusion distance for a dissolved-phase source < 1,000 µg/L benzene (no O_2 measurement)
- 5 ft. vertical separation distance between a dissolved-phase source < 1,000 µg/L and a building foundation (measured O_2 in soil gas ≥ 4%)

Scenario 4: Direct measurement of soil gas concentrations

Application of an additional attenuation factor of 1000x to risk-based soil-gas criteria (i.e. vapor sources) located 5 ft. from a building foundation

For each of these scenarios, screening criteria have been proposed that if met will identify the site as posing a low human health threat resulting from the vapor intrusion pathway. The screening criteria and low-risk scenarios are based on the science presented in this document; additional safety factors were incorporated as a policy decision. For the two un-weathered LNAPL scenarios (Scenarios 1 and 2), the current science indicates that soil vapors above an LNAPL source will attenuate within a distance of 20 feet or less. However the two LNAPL scenarios include an additional safety factor of 10 feet so that the exclusion criteria for these cases are set to 30 feet. This buffer distance should take into account any uncertainties with respect to water-table fluctuation. Likewise, in Scenario 3, the scientific studies and field data indicate that the risk of vapor intrusion is negligible for building foundations located more than 5 feet above plumes with much higher benzene concentrations (up to 15,000 μg/L in groundwater). Again, the proposed screening criteria incorporate additional safety factors which account for uncertainties in the water-table elevation. Management strategies to monitor and prevent groundwater from coming in contact with building foundations should, however, be considered in cases where the vertical separation distance between the building foundation and the dissolved-phase hydrocarbon source is < 5 ft. In Scenario 4, research indicates that soil gas concentrations will attenuate by more than 3 orders of magnitude within a vertical distance of 5 feet. However, the "bioattenuation factor" applied in Scenario 4 is conservatively defined at 3 orders of magnitude (1000-fold attenuation). The proposed bioattenuation factor (in Scenarios 3 and 4) also requires that measured O_2 concentrations in soil gas are greater than or equal to 4%. The practitioner should refer to local regulatory guidance for information on how to collect these measurements. Biodegradation has been shown to be significant at concentrations between 1 and 4 % (DeVaull, 2007). In conclusion, each of the scenarios, by design, had safety factors included and therefore the exclusion criteria will appear to be more conservative than would be otherwise indicated if only basing the results on the modeling results and field data presented in this document.

2 INTRODUCTION

It is well recognized that petroleum hydrocarbons rapidly biodegrade in the presence of O_2 (i.e., when conditions in the unsaturated zone are aerobic). The degree of biodegradation depends mainly on O_2 availability of and the O_2 demand created by the biodegradation reaction. The latter is largely a function of hydrocarbon source type (e.g., LNAPL or dissolved phase). Biodegradation can also be affected at soil moisture content, however, especially if less than the wilting point (i.e., a level sufficient to support plant growth) (Guyman 1997). Unsaturated-zone soils are seldom drier than the wilting point; however, with the exception of near surface soil layers under arid conditions (DeVaull, 1997).

Various researchers (Fischer et al., 1996; Lahvis et al., 1999; DeVaull, 2007; Davis, 2009; and Hartman, (2010) have shown that conditions in the unsaturated zone are aerobic, and that for "low-concentration" sources (weathered residual in soil and/or dissolved concentrations in groundwater), the degree of biodegradation is significant. At these sites, the demand for O_2 resulting from biodegradation generally exceeds O_2 availability. The hydrocarbon concentrations (mainly BTEX) decrease by several orders of magnitude over relatively short (e.g. <2 m) vertical distances. For low concentration hydrocarbon sources, the attenuation will tend to be significant very near the water table (i.e., capillary zone). These assertions are supported both by theory (modeling) (DeVaull, 2007, Abreu et. al. 2009, API, 2009) and by field observation (Lahvis and Baehr, 1996; API, 2009; Davis, 2009). Work by Abreu and Johnson (2005) predicts a greater degree of vapor attenuation at sites where the source is displaced laterally from the building foundation.

Researchers have also documented rapid biodegradation of petroleum vapors at sites underlain by LNAPL sources. At such UST sites, exclusion distances determined by analyzing benzene concentrations in soil gas have been estimated to be in the range of 8 to 15 feet (Davis, 2009; Hartman, 2010; Lahvis, 2011). The greater exclusion distance for LNAPL sources compared to dissolved-phase sources is largely related to the additional demand for O_2 (noted above) created by LNAPL sources and the tendency for

LNAPL sources to be distributed above the capillary zone. Lahvis and Baehr (1996) showed the capillary zone to be an active zone of biodegradation and hydrocarbon attenuation). The presence of residual-phase LNAPL can, however, be difficult to identify because LNAPL may not readily appear in groundwater monitoring wells. In such cases, one may rely on general LNAPL indicator "rules of thumb", including:

Presence of LNAPL

Direct evidence:

- current or historical evidence of LNAPL in soil (known release area) or at the water table (visible/reported in nearby groundwater monitoring wells)

Indirect evidence:

- hydrocarbon VOC concentrations in groundwater approaching (> 0.2) effective solubilities (Bruce et al., 1991) (e.g., benzene > 3 mg/L; BTEX or TPH gasoline range organics (GRO) > 20 mg/L; TPH diesel range organics (DRO) > 5 mg/L)
- total hydrocarbon VOC concentrations in soil of TPH GRO > 100 - 200 mg/kg(1); TPH DRO > 10 - 50 mg/kg) (see ASTM, 2006, Alaska DEC, 2011)[2]
- TPH vapor readings from a photo-ionization detector (PID) of > 1,000 ppm (recent gasoline releases), > 100 ppm (recent diesel/historic gasoline releases), and > 10 ppm (historic diesel releases) (Alaska DEC, 2011). Note that weathered LNAPL typically has a significantly reduced VOC content and therefore represents a lesser vapor intrusion risk than un-weathered NAPL.
- proximity (e.g., < 20 ft to a known release area)

It is important to note that although hydrocarbon VOC concentrations approaching effective solubility limits in groundwater can be used as an indirect indicator of residual-phase LNAPL, dissolved-phase hydrocarbon concentrations are not necessarily good metrics for the development of screening criteria (i.e., separation distances) or assessing the vapor intrusion risk potential. Benzene concentrations in soil-gas have shown to be poorly correlated with benzene concentrations in shallow groundwater (Lahvis, 2012). The poor correlation can be attributed to 1) the inability to accurately measure the dissolved-phase source (water-table) concentration (i.e., the actual hydrocarbon vapor source) using conventional ground-water monitoring wells screened across the water table, and 2) hydrocarbon biodegradation between the water table (dissolved-phase source) and the lowermost soil-gas sampling location. Soil-gas and ground-water concentrations are also expected to be poorly correlated in the presence of residual-phase LNAPL sources (Zemo, 2006). Screening (exclusion) distances should therefore be defined on the basis of source type (LNAPL and groundwater) rather than source

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[1] TPH (GRO) between 100 to 200 mg/kg may indicate may indicate the presence of LNAPL. TPH (GRO) less than 100 mg/kg is a good indication that there is no LNAPL present. The practitioner should refer to local regulatory guidance for TPH sampling and analysis.

[2] The primary driver for vapor intrusion is benzene. For petroleum-based fuels other than gasoline, benzene is not found at levels that would cause a vapor intrusion problem.

(groundwater) concentration. LNAPL and dissolved-phase hydrocarbon sources are unique with respect to their vapor intrusion risk potential for the following reasons:

1) Differences in hydrocarbon vapor diffusion and O_2 demand: hydrocarbon vapor diffusion (mass flux) in the unsaturated zone will be higher for LNAPL sources than dissolved-phase sources because LNAPL contains a higher source mass and is invariably distributed (by water-table fluctuations) above the capillary zone in lower moisture-saturated soil less resistant to vapor transport. The vapor mass flux for LNAPL source zones will also tend to be sustained for longer-periods of time given the larger contaminant mass compared to dissolved sources. The higher rates of vapor diffusion from LNAPL sources will be coupled with greater metabolic demand for O_2 associated with aerobic biodegradation.

2) Differences in vapor composition: vapors emanating from dissolved-phase sources are primarily BTEX and other aromatic hydrocarbons and fractionally water-soluble petroleum VOCs. Vapors emanating directly from LNAPL sources contain these constituents and a sizeable fraction of aliphatic and relatively insoluble VOCs, especially if the source is large or un-weathered.

The exclusion distances proposed in policy focus primarily on benzene, which is the primary risk driver for petroleum UST sites. Ethylbenzene and total petroleum hydrocarbon (TPH) data are included in this technical justification only for comparative purposes. Naphthalene is not considered. Rather, the exclusion criteria derived for benzene are assumed to be conservative for naphthalene, which is relatively less volatile than benzene (i.e., has a much lower solubility value and Henry's Law coefficient than benzene) and similarly susceptible to biodegradation (Anderson et al., 2008). Methyl tert-butyl ether (MTBE), which may be considered another potential VOC of concern for vapor intrusion in some regulatory jurisdictions, is also not considered. The exclusion of MTBE can be justified on the basis that no reports of MTBE as a constituent of concern for vapor intrusion are documented in the literature even though MTBE is routinely measured as part of soil-gas sampling (TO-15 air analyses). In addition, long-term (30-yr exposure duration) chronic inhalation risks from MTBE are not expected to occur a because of rapid attenuation of MTBE in source areas. In particular, McHugh et al. (2012) shows MTBE concentrations have decreased in ground water by an average of 85% from 2001 to 2011 in California post the phase out of MTBE as an oxygenate in gasoline in 2000 and its elimination on January 1, 2004.

3 TECHNICAL BACKGROUND – Discussion of Biodegradation Effects

This section presents the results of model studies and field data that support the proposed vapor intrusion exclusion criteria. The results are discussed first for "low-concentration" source cases followed by "high-concentration" sources cases.

3.1 Low-Concentration Sources (weathered residual in soil and/or dissolved concentrations in groundwater)

For purposes of this technical justification, low concentration sources at petroleum UST sites are defined as dissolved-phase hydrocarbon concentrations. Low concentration sources are therefore composed primarily of the more soluble (aromatic) VOC LNAPL constituents, benzene, toluene, ethylbenzene, xylenes, and naphthalene. Of these constituents, benzene is the primary risk driver for vapor intrusion because of its relatively higher toxicity and vapor migration potential. Note: weathered LNAPL is analogous to low-concentration sources in cases where the LNAPL is depleted of VOCs.

3.1.1 Model Studies

Results from numerical (3-dimensional) models (see Figures 3, 4 and 10 below[Abreu et al., 2009])indicate essentially complete attenuation of benzene soil gas concentrations (between 7 and 14 orders of magnitude – expressed as attenuation factors ⍰ < 1E-07) within 2 m to 3 m away from a relatively low (< 10 mg/L or 10,000,000 $\mu g/m^3$) benzene source concentration in an unsaturated sand.[3] The simulations also assumed biodegradation occurred only in the aerobic portion of the unsaturated zone (i.e., where O_2 concentrations exceed 1%). An aerobic biodegradation rate of 0.79 hr^{-1} was assumed for benzene, which is consistent with the geometric mean of published rates defined by DeVaull (2007). Note that while this degradation rate may seem high, the model only simulates biodegradation in the portion of the unsaturated zone where there is sufficient O_2 (> 1 %) to support biodegradation. The modeled hydrocarbon vapor source concentration, < 10 mg/L, is assumed to be consistent with a dissolved-phase source (see Abreu et al. [2009] – Figure 10). Lastly, the attenuation is expected to increase for a similar range of source concentrations and degradation rates in lower permeability soils (e.g., silty clay) (see Figure 19 from API, 2009) and for sources displaced laterally from building foundations (see Figure 9 from Abreu and Johnson, 2005). The attenuation increases for the latter scenario because hydrocarbon transport tends to be vertically upwards (toward the soil surface) rather than laterally towards the receptor. Hence, there is little potential for vapor intrusion to occur at sites where the dissolved-phase source is separated laterally from a building foundation.

The following figures show the results of the modeling studies:

- The figures from Abreu et al. (2009) (Figures 3 and 4) show benzene and O_2 profiles predicted by transport modeling for low-concentration vapor sources and two different foundation configurations (basement and slab, respectively) in a sand unsaturated zone for a reasonable approximation of the hydrocarbon biodegradation rate (⍰ = 0.79 hr^{-1}).

---

[3] A 10 mg/L hydrocarbon soil gas source would equate to a ~40 mg/L source of BTEX in groundwater assuming a vapor/aqueous phase partition coefficient of around 0.25 (Morrison, 1999).

Figure 3 from Abreu et al (2009).

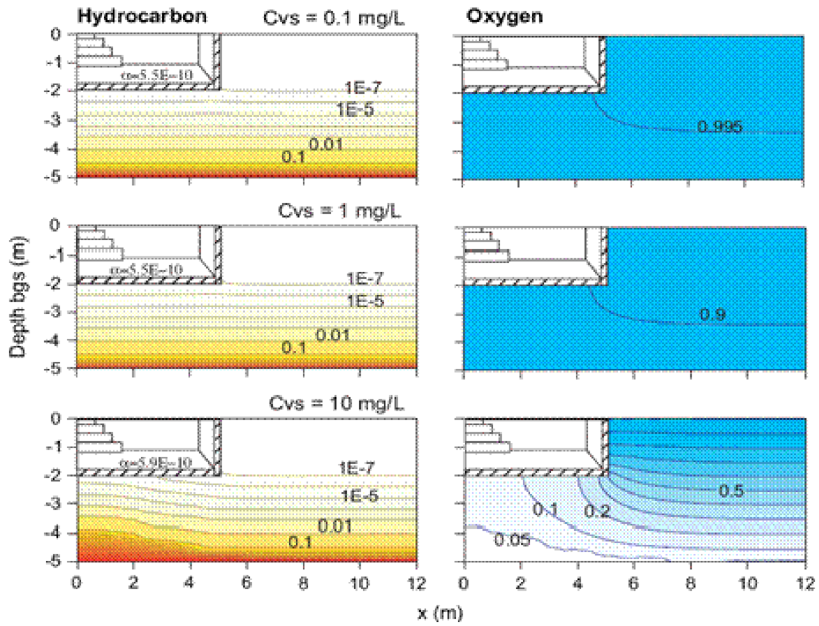


Figure 3. Effect of low vapor source concentration (Cvs) on soil-gas concentration distribution and vapor intrusion attenuation factors (α) for basement foundation scenarios and hydrocarbon biodegradation rate λ = 0.79 h^{-1}. Hydrocarbon and oxygen concentrations are normalized by source and atmospheric concentrations, respectively.

Figure 4 (Abreu et al., 2009)

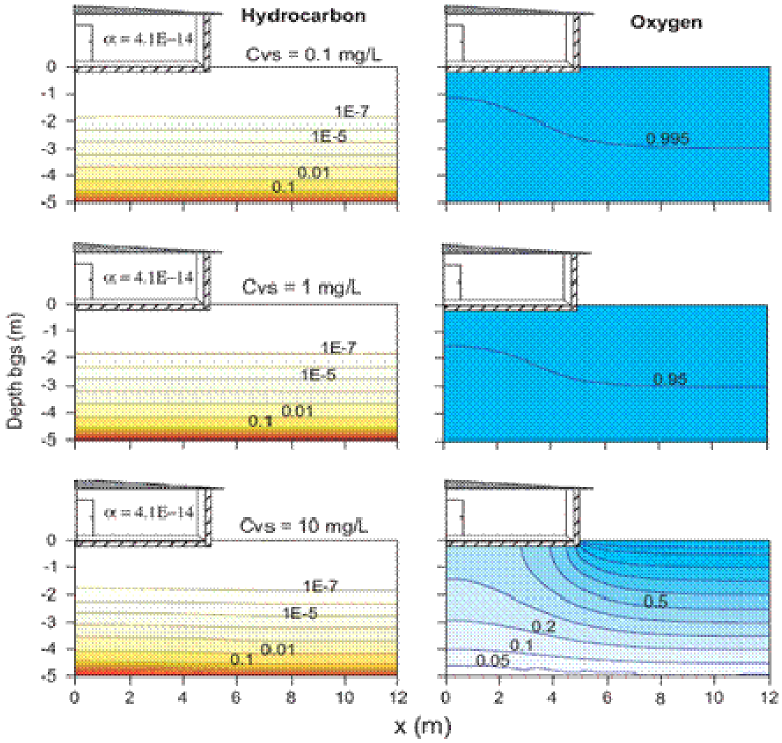


Figure 4. Effect of low vapor source concentration (Cvs) on soil-gas concentration distribution and vapor intrusion attenuation factors (α) for slab-on-grade foundation scenarios and hydrocarbon biodegradation rate λ = 0.79 h^{-1}. Hydrocarbon and oxygen concentrations are normalized by source and atmospheric concentrations, respectively.

- Figure 10 from Abreu et al. (2009) is a plot of the hydrocarbon (benzene) attenuation factor in the unsaturated zone versus source vapor concentration for a range of source/building foundation separation distances assuming a representative biodegradation rate (= 0.79 hr^{-1}) and a sand unsaturated zone:

Figure 10 from Abreu et al. (2009)

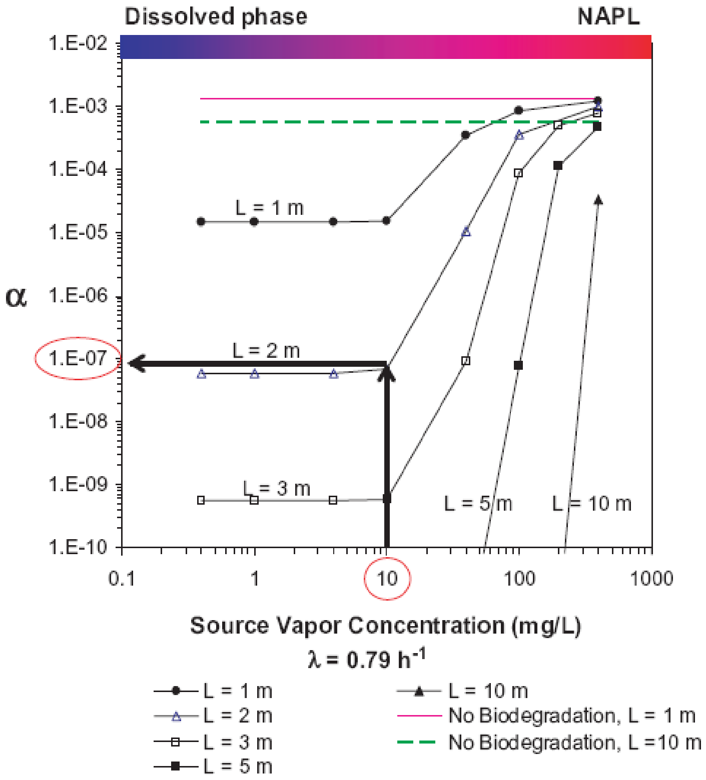


Figure 10. Use of the chart to select a semi-site-specific attenuation factor. For a source concentration of 10,000 μg/L and a source-building separation of 2 m, the attenuation factor would be about 1E-7.

- Figure 19 from API (2009) is a plot of the hydrocarbon (TPH-gasoline) attenuation factor in the unsaturated zone versus source vapor concentration for a range of source/building foundation separation distances assuming a representative biodegradation rate and two soil types, sand and silty clay:

Figure 19 from API (2009)

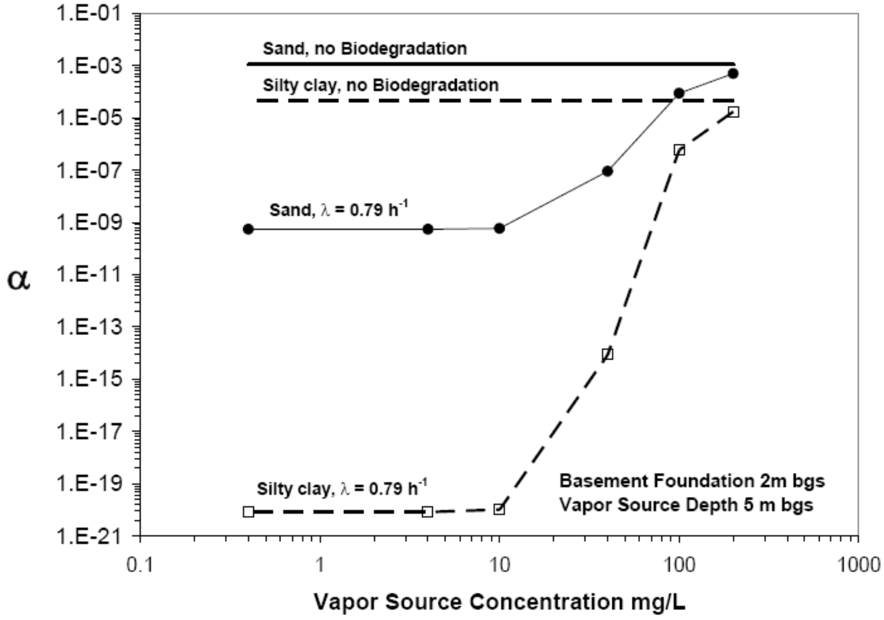


Figure 19—Attenuation factors as a function of soil type and vapor source concentration for a source located at 5 m bgs (3 m below a basement foundation). The graph present results for no biodegradation scenarios and biodegradation scenarios with a first-order biodegradation rate $\lambda = 0.79\ h^{-1}$. Qs (sand) = 3.7 L/min and Qs (silty clay) = 0.05 L/min.

- Figure 9 from Abreu and Johnson (2005) is a plot of the attenuation factor in the unsaturated zone versus source edge-building separation distance predicted in a sand unsaturated zone for a slab-on-grade building foundation. Biodegradation was not considered in the model analysis.

Figure 9 from Abreu and Johnson (2005)

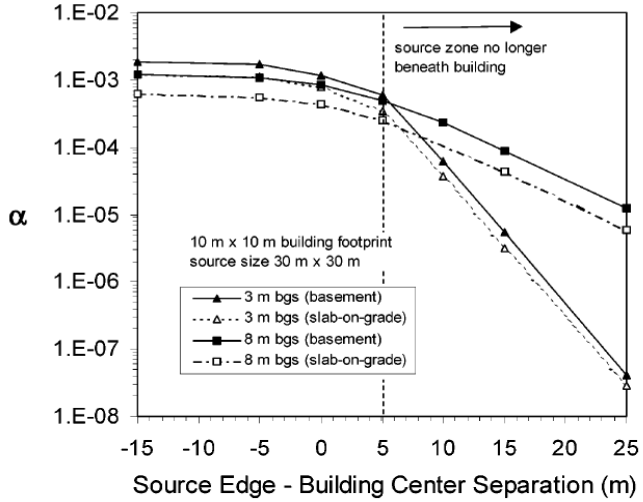


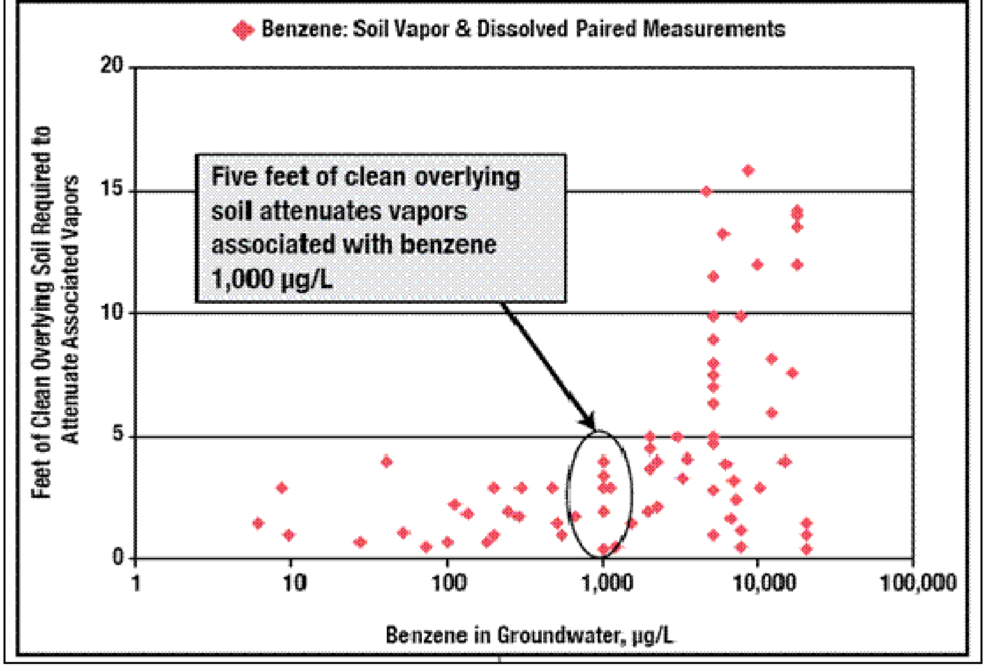
FIGURE 9. Changes in vapor attenuation coefficient (α) with vapor source—building separation and vapor source depth for basement and slab-on-grade foundation scenarios.

3.1.2 Field Data

Two hydrocarbon soil-gas databases were used to support the development of exclusion distance criteria. One was compiled by Davis (2009) and the other by Wright (2011). The cited databases are publically available upon request. Davis (2009) compiled the database from measurements at 58 UST, terminal, and manufacturing sites across several states, including California. The Wright (2011) database includes soil-gas data collected from 124 additional UST, terminal, and manufacturing sites in Australia. Both databases include soil-gas data collected from on and off-site locations. Approximately 16% of the soil-gas data are measurements taken directly below building foundations (i.e., sub-slab). The field data support the model results discussed in the previous section. An analysis by Davis (2009) indicates that benzene concentrations in soil gas are completely attenuated within 5 feet or less of groundwater containing up to 6 mg/L (or ~1,500,000 μg/m^3 vapor phase equivalent[4]) benzene (see Figure 5 below from Davis, 2009). The analysis includes data from “non-UST” locations.

Figure 5 from Davis (2009)

Figure 5: Thickness of Clean Overlying Soil Required to Attenuate Benzene Soil Vapors Associated with Various Dissolved Source Strengths (all soil types)



It is important to note in Figure 5, that the exclusion distance (and vapor intrusion risk potential) is relatively independent of the benzene source concentration over the approximate range of dissolved phase concentrations up to 6,000 μg/L. The development of more conservative groundwater

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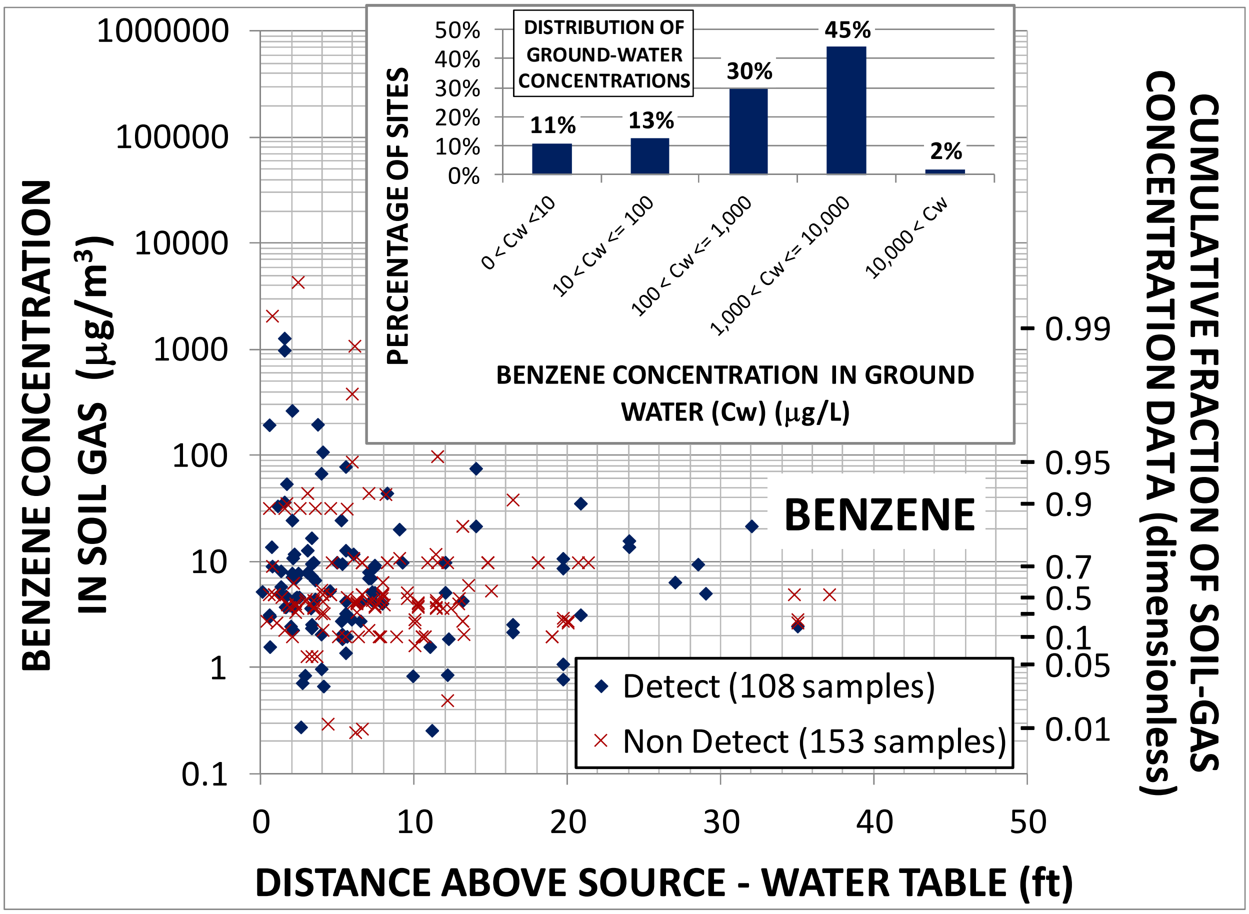
[4] Assuming equilibrium partitioning between soil-gas and groundwater and a Henry’s Law coefficient of 0.25 m^3/m^3 for benzene. The Henry’s Law constant for benzene is only expected to only vary by a factor of 2 (0.09 - 0.18) for anticipated soil temperatures ranging from at 5°C to 20°C (Baehr et al., 1999).

concentration-based exclusion distances (e.g., specific exclusion distance criteria for 100 µg/L and 1,000 µg/L sources) was a policy decision.

Davis (2009) did not screen out sites with potential residual LNAPL sources above the water table (i.e. LNAPL in soil). Note that residual LNAPL in soil and free-phase LNAPL on groundwater will pose similar vapor-intrusion risks. The latter are sites where LNAPL is observed in groundwater monitoring wells located in the source area. However, Davis (2009) found that the thickness of "clean" soil required to fully attenuate vapors to health-protective concentrations (i.e., the exclusion distance) decreased from ~15 feet (Figure 5) to 8 feet when accounting for residual-phase LNAPL sources above the water table (Davis 2010 – see Figure from Davis in Section 3.2.2).

Lahvis (2012) analyzed soil-gas data collected above dissolved-phase sources where efforts were taken to identify and screen out sites with LNAPL above the water table (i.e LNAPL in soil). The analysis filtered out sites with either direct evidence of LNAPL (current, historical) or indirect evidence of LNAPL (soil-gas measurements collected near potential sources (i.e., locations within 20 ft of USTs and dispensers). The analysis did, however, include soil-gas data from sites with dissolved-phase (source) concentrations up to 15 mg/L benzene. Lahvis (2012) included these additional data to assess an "upper bound" on exclusion distances for dissolved-phase sources, realizing that dissolved-phase concentrations greater than 3 mg/L benzene and 20 mg/L BTEX may potentially indicate the presence of a residual-phase LNAPL source (Bruce et al. , 1991). In other words, Lahvis (2012) included soil-gas data from sites with potential LNAPL sources to be conservative in estimating the exclusion distances for dissolved-phase sources. The Lahvis (2012) study included soil-gas data from both Davis (2009) and Wright (2011). Lahvis (2012) shows that benzene in soil vapor is attenuated below a relatively conservative soil-gas screening level of 30 µg/m^3 for dissolved benzene sources located 5 vertical feet or greater from the receptor. Note that more than half of the soil-gas measurements were taken from sites with source concentrations of benzene dissolved in groundwater ranging from 1 to 15 mg/L.

Figure from Lahvis (2012)



The results shown in the figure from Lahvis (2012) were then used to define exclusion distance criteria based on the probability[5] of the measured soil gas concentration being less than specified (vapor intrusion) screening level concentrations for benzene in soil gas of 30, 50 and 100 µg/m^3. These values are consistent with current U.S. state regulatory soil-gas screening limits for benzene which range from approximately 3 to 300 µg/m^3 (see EnviroGroup Limited - http://www.envirogroup.com/links.php). The data were then sorted in a cumulative distribution of specified vertical separation distances from the source (e.g., ≥ 0, ≥ 2, … ≥ 10 ft). The results are shown in the following figure:

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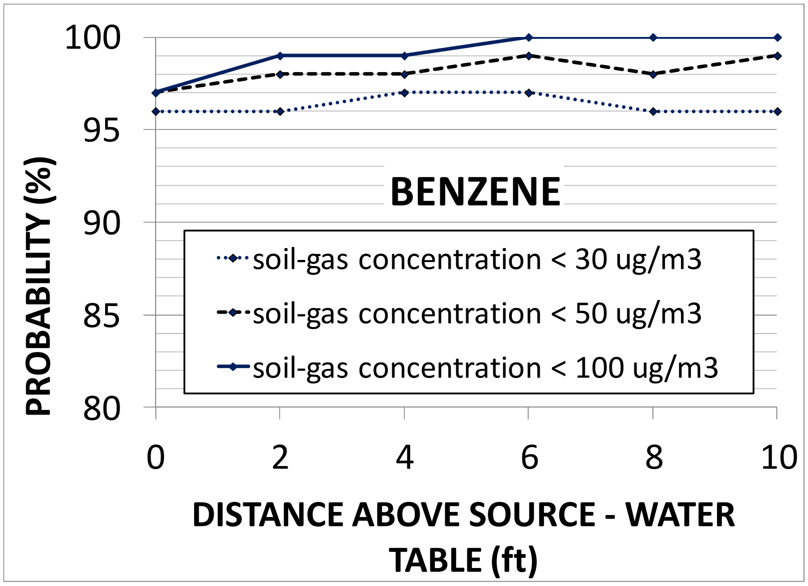
[5] Probability estimated from the concentration distribution calculated by non-parametric Kaplan-Meier method (Kaplan and Meier, 1958)

Figure from Lahvis (2012)



The results indicate that the probability of observing benzene vapor concentrations in excess of a conservative screening level (e.g., 30 µg/m^3) at distances greater than 5 ft above the dissolved phase source at UST sites is less than 5%. The water table would have to be essentially in contact with a building foundation for there to be a potential concern for vapor intrusion for this class of low concentration sites. Note there is limited sensitivity to the benzene soil-gas screening limit over the specified range (30 – 100 µg/m^3).

The data from which the vertical exclusion distances were derived encompass a broad range of environmental site conditions, geographic retail markets, and a 14-year time span of sample collection (from 1997 to 2011). The exclusion distances (0 ft for dissolved-phase sources and 13 ft for LNAPL) are thus deemed applicable for the vast majority of petroleum UST sites, including those with differing soil types, land-surface covers (including sub-slab and pavement), subsurface temperatures, and fuel types/compositions. Approximately 67% of the soil-gas samples in the Lahvis (2012) database were collected at UST sites in Utah and Australia where relatively low soil-moisture conditions are likely to have been present. The empirical study comprised data collected throughout the year at UST sites in Utah, Maine, Minnesota, Canada, Australia and California suspected of having highly variable subsurface soil temperatures. The soil conditions at these sites are thus assumed to represent soil conditions encountered at the vast majority of relatively arid UST sites in California.

Additional validation may, however, be warranted at certain unusual sites not statistically captured in the database or by the Lahvis (2012) analysis. These sites include those with high organic matter soils (e.g., peat), a really extensive building foundations at land surface (e.g., large commercial facilities or apartment complexes), and high (85%) ethanol content fuel (e.g., E85) releases.

3.1.3 Summary of Low Concentration Sources

In summary, model and field data from UST petroleum release sites shows minimal vapor-intrusion-to-indoor air risk above dissolved-phase only hydrocarbon sources. At low-concentration sites, benzene, the primary risk driver for vapor intrusion, will be attenuated below conservative soil-gas screening limits within 5 feet above the water table.

3.2 High-Concentration Sources (un-weathered residual in soil and/or free-phase LNAPL on groundwater)

3.2.1 Model Studies

As shown in the attached figures (Figures 5 and 7 from Abreu et al. [2009]), benzene is predicted to completely attenuate in the unsaturated zone above an LNAPL source within ~ 7m (20 ft) of the source[6]. Abreu et al (2009) used benzene to represent the greatest potential risk posed by soil vapor from an un-weathered LNAPL vapor source. This LNAPL source will primarily consist of aliphatic hydrocarbons. The model is assumed to be conservative when considering benzene biodegradation assumptions (see note 7 below).

Figure 5 (modified) from Abreu et al. (2009)

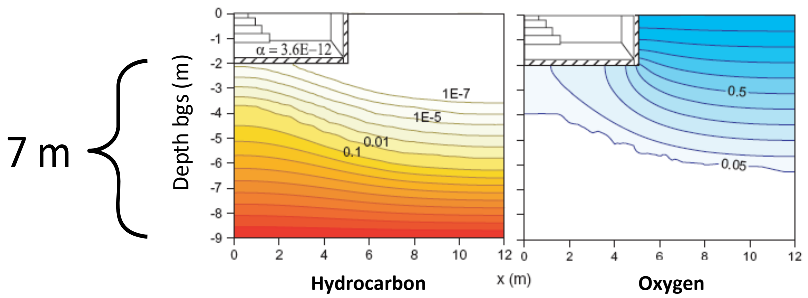


Figure 5. Effect of source depth on the soil-gas concentration distribution and vapor intrusion attenuation factors (α) for basement scenarios with a high vapor source concentration of 100,000 μg/L and biodegradation rate $\lambda = 0.79\ h^{-1}$. Hydrocarbon and oxygen concentrations are normalized by source and atmospheric concentrations, respectively.

Figure 7 (modified) from Abreu et al. (2009)

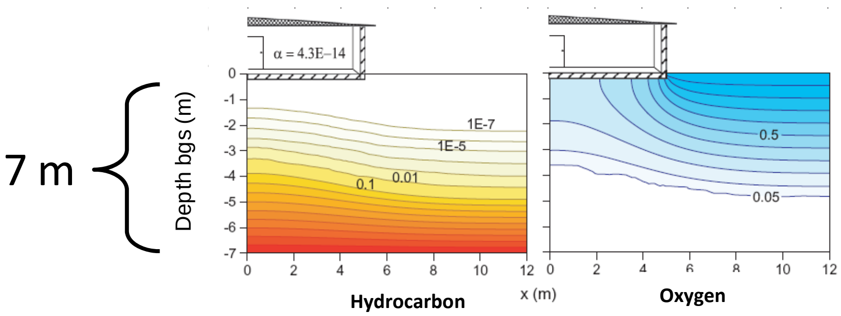


Figure 7. Effect of building type on soil-gas concentration distribution for high vapor source concentration (100,000 μg/L) and biodegradation rate $\lambda = 0.79\ h^{-1}$. Hydrocarbon and oxygen concentrations are normalized by source and atmospheric concentrations, respectively.

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[6] Note Figures 5 and 7 from Abreu et al. (2009) were slightly modified to highlight the technical justification.

Vapor attenuation is predicted to increase for LNAPL sources displaced laterally from the basement foundation (Abreu and Johnson, 2005).

3.2.2 Field Data

A recent analysis of a soil-gas database by Davis (2010) indicates that the model-predicted attenuation cited above is conservative. Davis (2010) found source-receptor separation distances of only 8 ft. attenuated soil-gas vapors associated with benzene and TPH from LNAPL sources to below health-risk screening criteria (see the following figure from Davis [2010]). The Davis (2010) analysis accounts for residual LNAPL sources in the unsaturated zone.

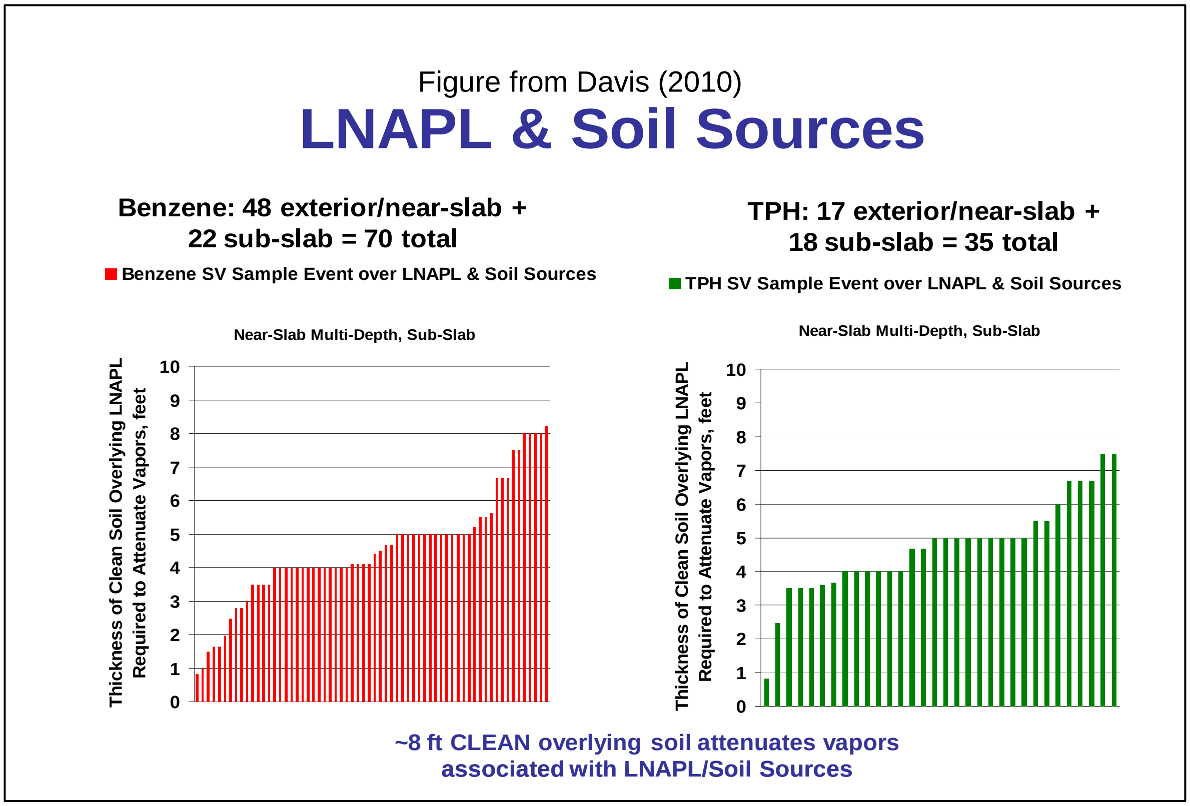


Figure from Davis (2010)

LNAPL & Soil Sources

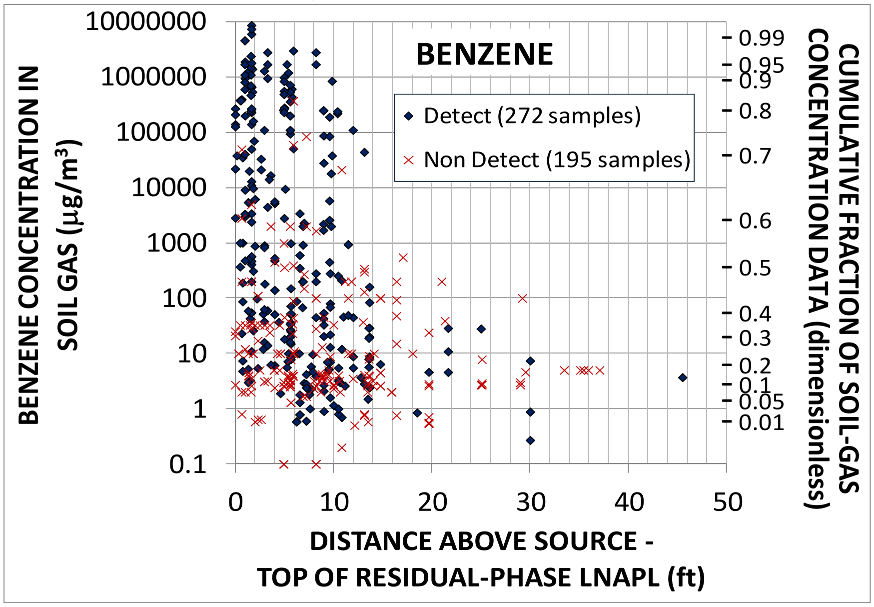
Benzene: 48 exterior/near-slab + 22 sub-slab = 70 total

TPH: 17 exterior/near-slab + 18 sub-slab = 35 total

~8 ft CLEAN overlying soil attenuates vapors associated with LNAPL/Soil Sources

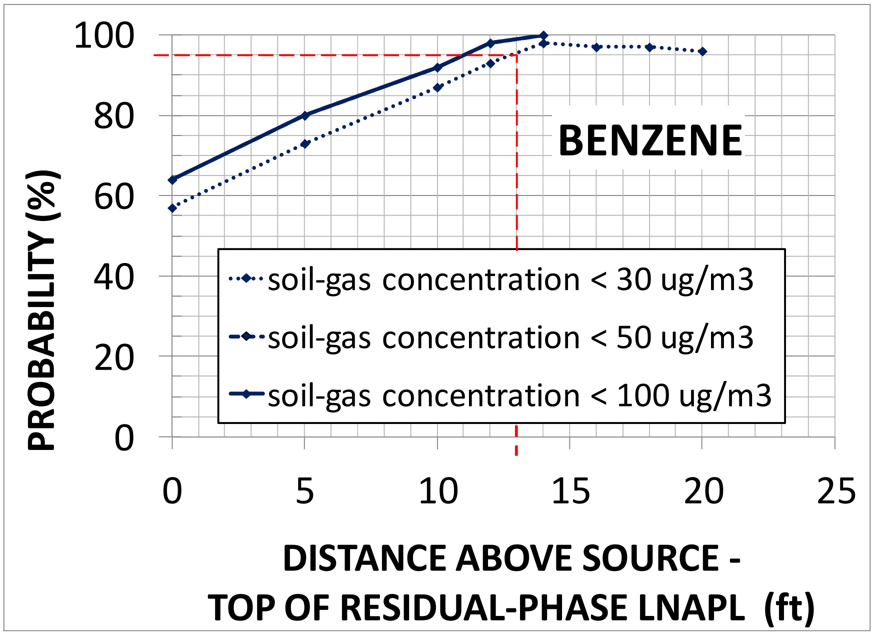
In addition, Lahvis (2012) demonstrates in the following figure that benzene concentrations in soil gas generally decrease by more than 4 orders of magnitude at source-receptor separation distances of > 13 feet at LNAPL sites:

Figure from Lahvis (2012)



From a conditional probability standpoint, benzene concentrations in soil gas will attenuate below 30 µg/m^3 at distances of >~ 13 ft above the source in greater than 95% of cases.

Figure from Lahvis (2012)



Again, lateral separation exclusion distances would be expected to be less than the vertical exclusion distances for the reasons previously presented. As noted in Lahvis (2012), the exclusion distance estimate is also relatively insensitive to the presence/absence of a building foundation at land surface.

This is an important observation with respect to managing risks associated with future building construction.

3.2.2 Summary

Most recent field data analyses indicate 8 to 13 feet of clean soil (soil with no LNAPL present) between source and receptor is sufficient to reduce soil-vapor concentrations to below health-protective levels for the vapor-intrusion-to-indoor air pathway at sites with LNAPL sources in either soil or groundwater.

3.3 Technical Background Conclusions

Researchers have demonstrated that soil-vapor benzene concentrations above low-concentration sources attenuate up to 6 orders of magnitude in the unsaturated zone within short vertical distances (e.g., < 5 ft) due to biodegradation. Biodegradation is sufficient to essentially eliminate these sites from further vapor intrusion consideration.

At sites with high concentration sources (e.g., un-weathered LNAPL sources), 8 to 13 feet of clean soil (i.e. TPH <100 mg/kg) are required to fully attenuate hydrocarbon vapors to health-protective concentrations for the vapor-intrusion-to-indoor air pathway. The attenuation due to biodegradation would be equally or more significant for LNAPL sources separated laterally from building foundations (i.e. a shorter distance would be required for attenuation to health-protective concentrations).

The use of soil-gas data to support the development of vapor intrusion guidance for petroleum hydrocarbon site screening is relatively new. Consequently, the technical justification includes several references to non-peer-reviewed literature. The work of Lahvis (2012) has recently been documented and is intended for publication in peer-reviewed literature. The study is being used to support the development of vapor intrusion guidance for US EPA Office of Underground Storage Tanks. Although the analyses are subject to change as a consequence of the peer review, the non peer-reviewed attachments are based on sound scientific knowledge and fundamental to the validation of model theory and development of vapor intrusion guidance. It is important to consider these “state of the science” results in the development of rational, technically defensible, approaches to vapor intrusion risk assessment. Please note that the Stakeholder Group that developed the Low-Threat UST Policy Petroleum considered the cited technical sources when developing the vapor-intrusion scenarios and associated risk criteria presented in the Low-Threat Policy. In addition*, as a statewide policy consideration*, the Stakeholder Group applied source-to-receptor separation distance and source concentration safety factors that make the proposed vapor-intrusion-to-indoor-air screening criteria *more conservative* than they would otherwise be if considering the scientific literature alone. These safety factors include greater separation distances and lower threshold concentrations than those found by researchers to be health protective.

4 THE FOUR LOW-THREAT VAPOR INTRUSION SCREENING SCENARIOS

The Stakeholder Group convened by the SWRCB considered the available current and relevant scientific studies when developing the following low-threat vapor-intrusion-to-indoor air criteria. The four basic vapor-intrusion scenarios are:

Scenario 1: Un-weathered LNAPL on groundwater

30 ft vertical source/building separation (exclusion) distance for un-weathered (residual or free-phase) LNAPL on groundwater

Scenario 2: Un-weathered LNAPL in soil

30 ft lateral and vertical source/building separation (exclusion) distance for an un-weathered LNAPL (residual or free-phase) LNAPL source in soil and a building foundation

Scenario 3: Dissolved phase benzene concentrations in groundwater

- 5 feet vertical separation distance between a dissolved-phase source < 100 µg/L benzene and a building foundation (no oxygen (O_2) measurement)
- 10 feet vertical exclusion distance for a dissolved-phase source < 1,000 µg/L benzene (no O_2 measurement)
- 5 ft. vertical separation distance between a dissolved-phase source < 1,000 µg/L and a building foundation (measured O_2 in soil gas > 4% [7])

Scenario 4: Direct measurement of soil gas concentrations

Application of an additional thousand-fold biodegradation attenuation factor to risk-based soil-gas concentration criteria (CHHSLs) when the source is located more than 5 feet from a building foundation

Scenarios 1 and 2 are will usually be associated with "high"-concentration sources. Scenario 3 is associated with a "low" concentration source, and Scenario 4 may be associated with either "low" or "high" concentration sources. The following section details the technical justification(s) for each of the sets of low-threat exclusion criteria expressed in the four scenarios.

The vapor-intrusion exclusion distance criteria determined for benzene are assumed to be health-protective for other potential hydrocarbon VOCs, such as ethylbenzene and naphthalene. For ethylbenzene, this assumption is based on 1) ethylbenzene having similar source concentrations and fate and transport properties as benzene (Abreu et al., 2009), and 2) a strong correlation between benzene and ethylbenzene concentrations in soil-gas measured concurrently from the same soil-gas probe (see following figure from Lahvis [2012]):

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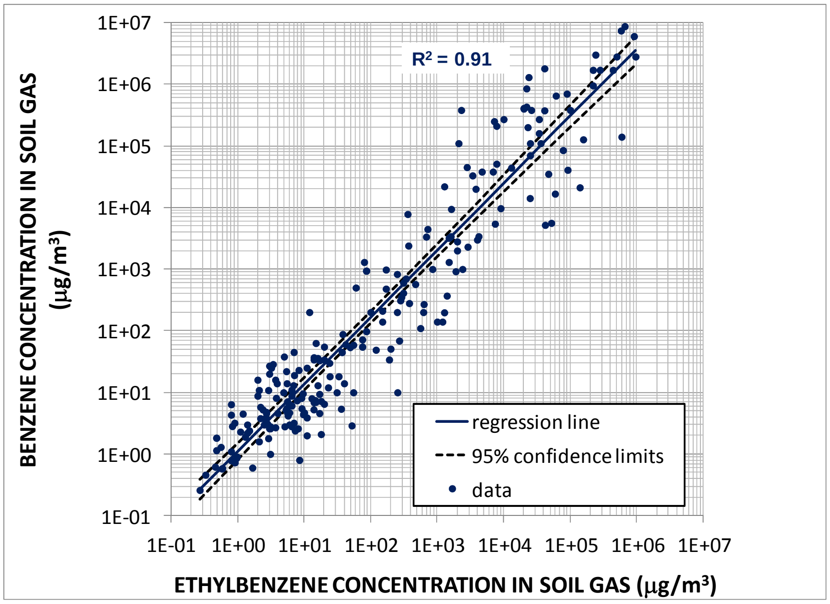
[7] 4% refers to 40,000 ppmv. O_2 concentrations in soil gas sufficient to support aerobic mineralization are reported to be in the range of 1 to 4 % (DeVaull, 2007).

Figure from Lahvis (2012)



The exclusion distance criteria determined for benzene are assumed to be conservative for naphthalene because 1) naphthalene is typically present in gasoline at lower fractions as benzene, 2) naphthalene is likely present at very low concentrations (mass fraction of 0.0026) in diesel (Potter and Simmons, 1998), and 3) naphthalene is less volatile, and has similar (if not, higher) degradation rates as benzene (GSI, 2010).

4.1 Scenario 1: Un-weathered LNAPL on Groundwater

30 ft vertical source/building separation (exclusion) distance for un-weathered (residual or free-phase) LNAPL on groundwater

The proposed 30 feet exclusion distance[8] is conservative based on:

- Model theory shows full attenuation within 7 m (~ 20 ft) of a high concentration LNAPL source assuming reasonable approximations of the biodegradation rate (see Figures 5 and 7 below from Abreu et al., 2009)[9]. The use of benzene to represent an un-weathered LNAPL vapor source (which will primarily consist of aliphatic hydrocarbons) is assumed to be conservative with respect to benzene biodegradation assumptions (linked to O_2 availability)[10].

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[8] The top of the residual-phase source can generally be assumed to be consistent with the historic high water-table elevation.

[9] Note Figures 5 and 7 from Abreu et al. (2009) were slightly modified to highlight the technical justification

[10] In this model, biodegradation is linked to O_2 availability. Biodegradation is not simulated when O_2 concentrations in the unsaturated zone fall below 1%. Relative to benzene, aliphatic hydrocarbons are less susceptible to biodegradation because they partition less to the aqueous phase (pore water) where biodegradation takes place. Simulating LNAPL with a single benzene source will thus be conservative with respect to O_2 demand (and benzene biodegradation) compared to simulating LNAPL using a primarily aliphatic hydrocarbons.

Figure 5 (modified) from Abreu et al. (2009)

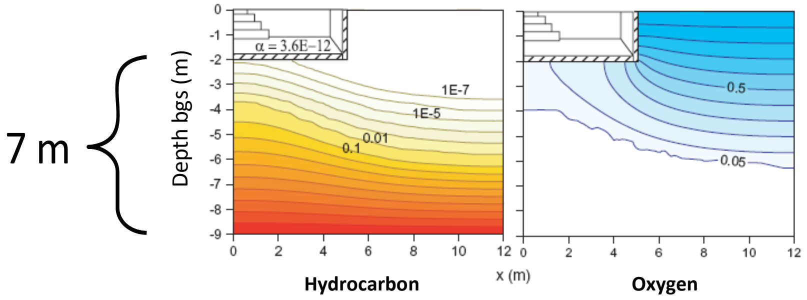


Figure 5. Effect of source depth on the soil-gas concentration distribution and vapor intrusion attenuation factors (α) for basement scenarios with a high vapor source concentration of 100,000 μg/L and biodegradation rate λ = 0.79 h^{-1}. Hydrocarbon and oxygen concentrations are normalized by source and atmospheric concentrations, respectively.

Figure 7 (modified) from Abreu et al. (2009)

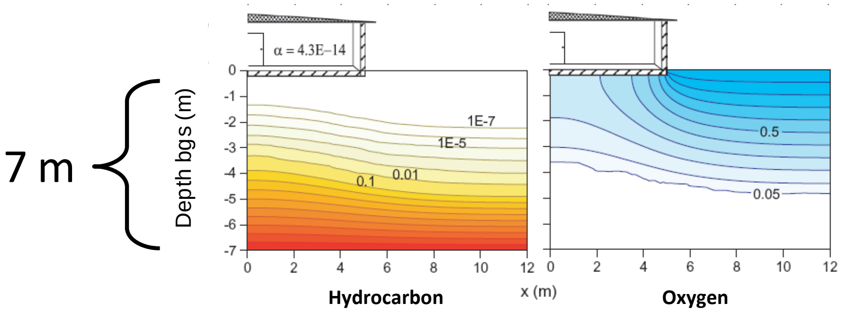


Figure 7. Effect of building type on soil-gas concentration distribution for high vapor source concentration (100,000 μg/L) and biodegradation rate λ = 0.79 h^{-1}. Hydrocarbon and oxygen concentrations are normalized by source and atmospheric concentrations, respectively.

- For LNAPL and residual sources, field (soil-gas) data show full attenuation within 8 ft of the source (see figure, below, from R. Davis [2010] – also published in Hartman [2010]).

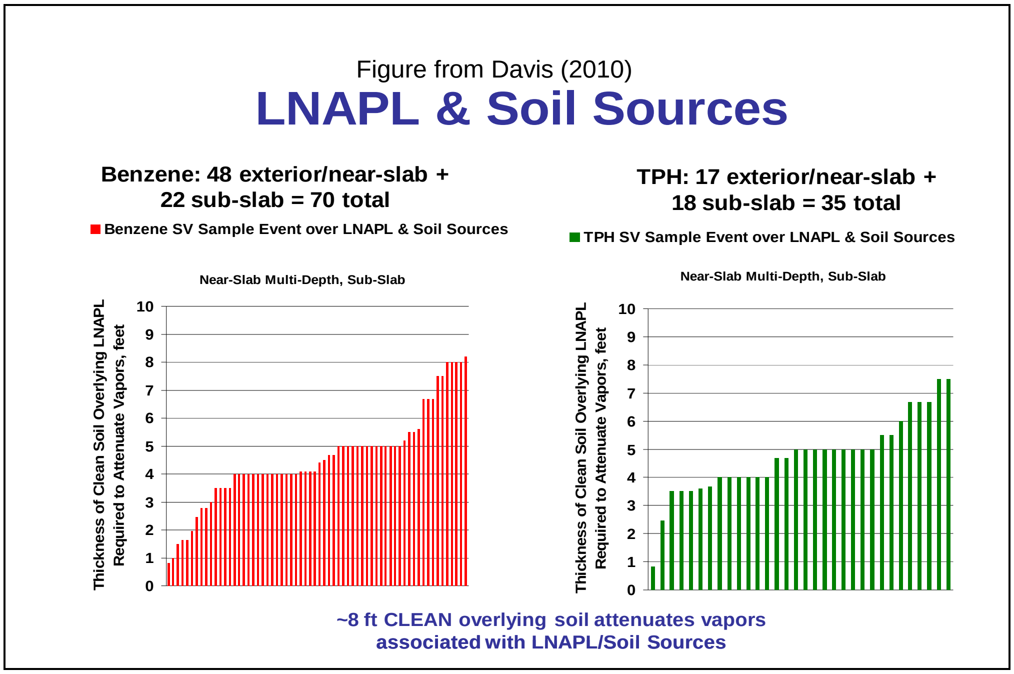


Figure from Davis (2010)

LNAPL & Soil Sources

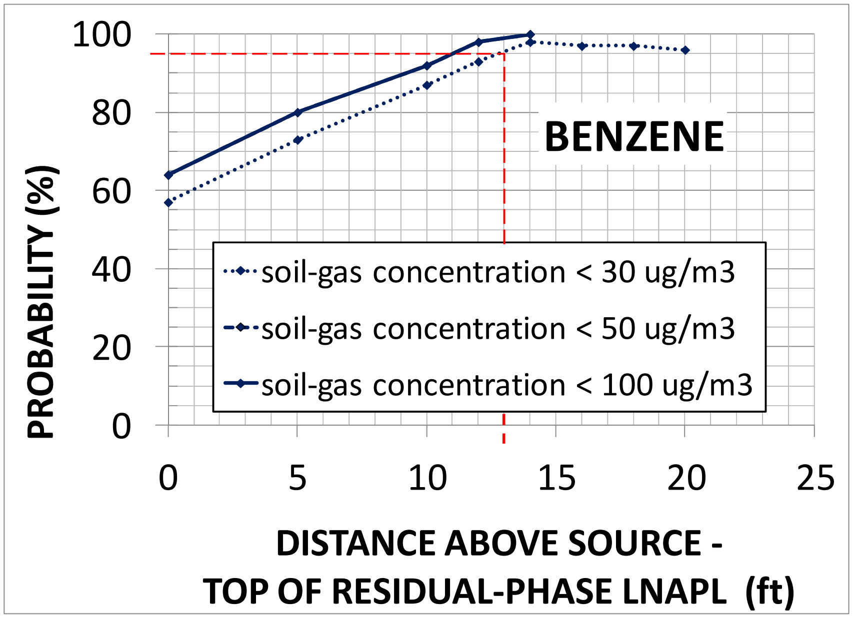
Benzene: 48 exterior/near-slab + 22 sub-slab = 70 total

TPH: 17 exterior/near-slab + 18 sub-slab = 35 total

~8 ft CLEAN overlying soil attenuates vapors associated with LNAPL/Soil Sources

The following figure from Lahvis (2012) shows a greater than 95% probability that benzene concentrations in soil gas will attenuate below a conservative screening level for benzene in soil gas of 30 µg/m^3 (alternatively, a < 5 % probability of observing benzene concentrations > 30 µg/m^3) at distances of > ~13 ft from a LNAPL (residual or free-phase) source.

Figure from Lahvis (2012)



4.2 Scenario 2: Un-weathered LNAPL in Soil

30 ft lateral and vertical source/building separation (exclusion) distance for an un-weathered LNAPL (residual or free-phase) LNAPL source in soil and a building foundation

The same technical justification provided for Scenario 1 applies to Scenario 2. The proposed 30 feet lateral off-set distance is even more conservative for sources displaced laterally as indicated in the following figure from Abreu and Johnson (2005). For example, an additional order of magnitude of attenuation is predicted for plume centerlines displaced 10 m (~30 ft).

Figure 9 from Abreu and Johnson (2005)

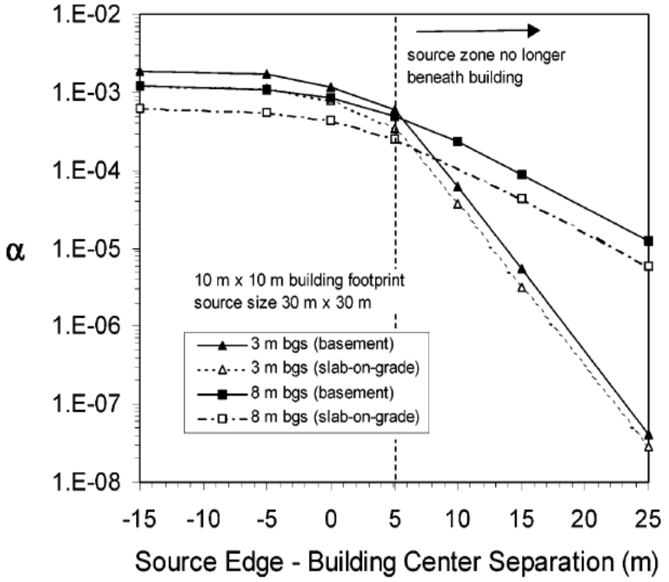


FIGURE 9. Changes in vapor attenuation coefficient (α) with vapor source—building separation and vapor source depth for basement and slab-on-grade foundation scenarios.

As discussed in the technical background section 3.2.2, 13 feet is more than adequate to fully attenuate vapors derived from LNAPL sources in soil and groundwater; therefore providing a 30-ft lateral distance screening criteria provides an additional safety factor.

4.3 Scenario 3: Dissolved Phase Benzene Concentrations in Groundwater

- **5 ft. vertical separation distance between a dissolved-phase source < 100 µg/L benzene and a building foundation (no oxygen (O_2) measurement)**
- **10 ft. vertical exclusion distance for a dissolved-phase source < 1,000 µg/L benzene (no O_2 measurement)**
- **5 ft. vertical separation distance between a dissolved-phase source < 1,000 µg/L and a building foundation (measured O_2 in soil gas ≥ 4% or 40,000 ppm_v)**

These separation distances are conservative with respect to protecting human health based on the following:

- Complete attenuation (~ 1E-07) is predicted within 2 m (6 ft.) of a soil gas source of benzene < 10 mg/L (or or 10,000,000 µg/m^3) (assumes an approximate 40 mg/L dissolved phase benzene concentration, based on an approximation of benzene partitioning between soil gas and groundwater [dimensionless Henry's Law constant = 0.25] - see attached Figure 10 from Abreu et al. [2009][11]). Even greater hydrocarbon attenuation (lesser exclusion distances) is predicted for dissolved-phase sources in other less permeable (e.g., silty clay) unsaturated zone systems (Abreu et al, 2009). The attenuation is complete for the entire vapor (dissolved-phase) concentration range. The dissolved phase concentrations (especially) (i.e., 100 µg/L) and proposed exclusion distance specified in this scenario are therefore assumed to be very conservative. Note: in the figure below, “L” is the distance to the foundation from the source.

Figure 10 from Abreu et al. (2009)

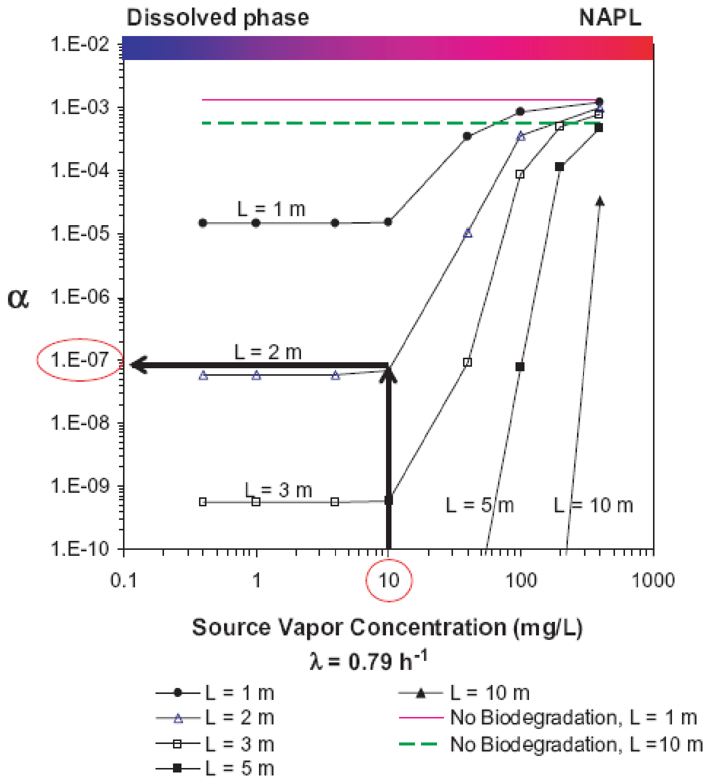


Figure 10. Use of the chart to select a semi-site-specific attenuation factor. For a source concentration of 10,000 µg/L and a source-building separation of 2 m, the attenuation factor would be about 1E-7.

- Model theory shows > 9 orders of magnitude (i.e. complete) attenuation (for reasonable approximations of the biodegradation rate ⍰ = 0.79 hr^{-1}) within a source/building separation distance of L=3 m (10 ft) in a sand unsaturated zone (Abreu et al. (2009)). This magnitude of attenuation is applicable for a benzene vapor source < ~10 mg/L (10,000,000 µg/m^3)(or ~40 mg/L dissolved phase source in groundwater assuming reasonable approximations for benzene partitioning between soil gas and groundwater (i.e., a dimensionless Henry’s Law constant = 0.25). Even greater hydrocarbon attenuation (lesser exclusion distances) is predicted for dissolved-phase sources in other less permeable (e.g., silty clay) unsaturated zone systems

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[11] Note figure from Abreu et al. (2009) was slightly modified to highlight the technical justification

(Abreu et al, 2009). The attenuation is complete for the entire vapor (dissolved-phase) concentration range. The dissolved phase concentrations (especially) (1,000 µg/L) and proposed exclusion distance specified in this scenario are therefore assumed to be very conservative. Note: in the figure below, “D” is the overall source depth and “L” is the distance to the foundation from the source.

Figure 6 from Abreu et al. (2009)

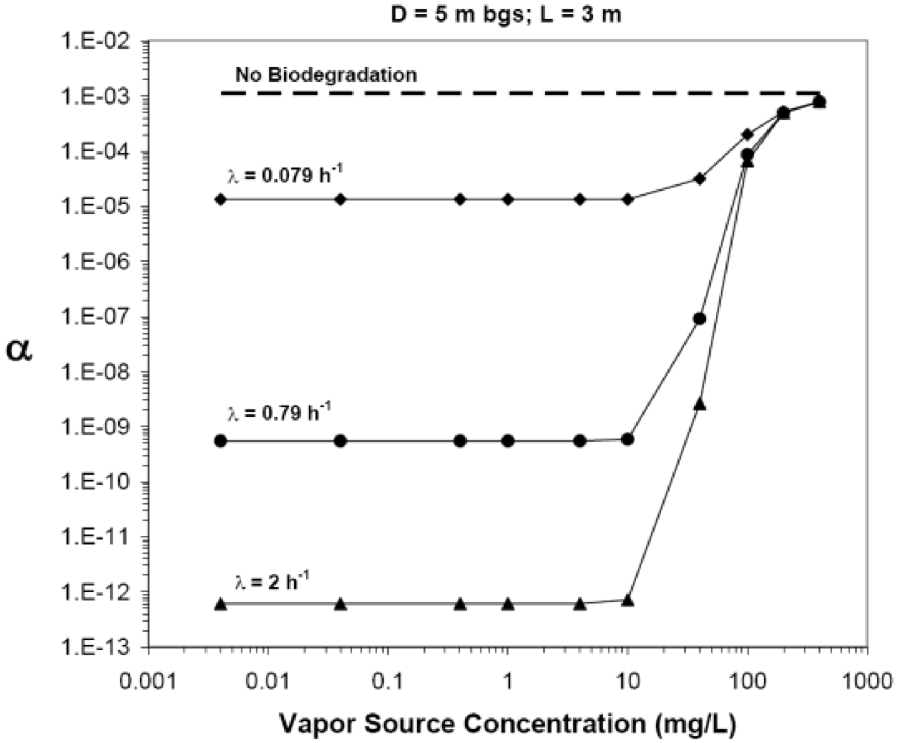

Figure 5—Influence of soil vapor source concentration and first-order biodegradation rates (λ) on vapor intrusion attenuation factors (α) for basement scenarios, homogeneous sand soil and source depth (D) of 5 m bgs (source-foundation separation L = 3 m).

- Field soil-gas data show complete soil-gas attenuation within 5 feet above benzene concentrations in groundwater of up to 6 mg/L (Davis, 2009).

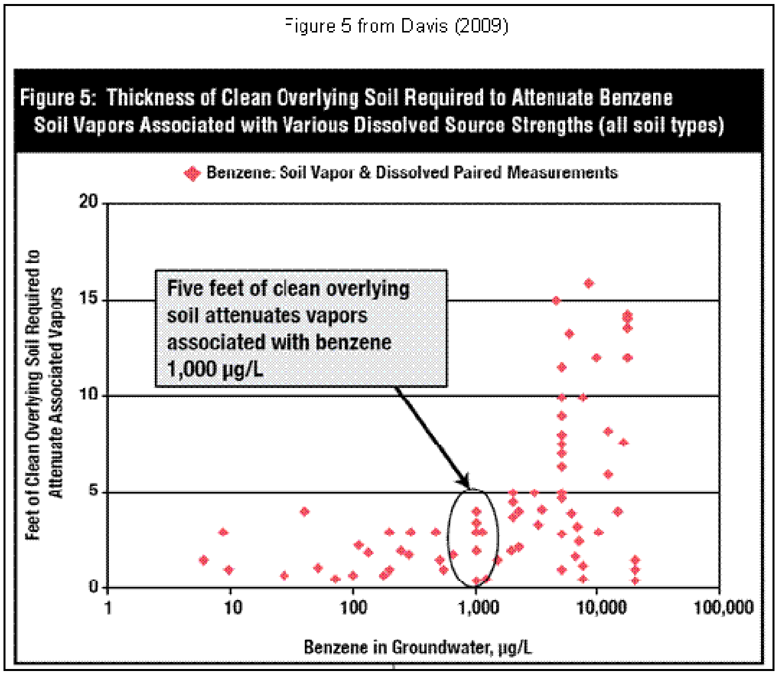
Figure 5 from Davis (2009)

Figure 5: Thickness of Clean Overlying Soil Required to Attenuate Benzene Soil Vapors Associated with Various Dissolved Source Strengths (all soil types)

- Field (soil-gas) data from Davis (2009) and Wright (2011) show benzene concentrations in soil gas attenuate below 80 µg/m^3 (see Figure 1) and 20 µg/m^3 (see Figure 2) within 10 feet above the water table for dissolved-phase benzene concentrations up to 1,000 µg/L and 100 µg/L, respectively at petroleum UST release sites.

Figure 1 - Lahvis (written communication)

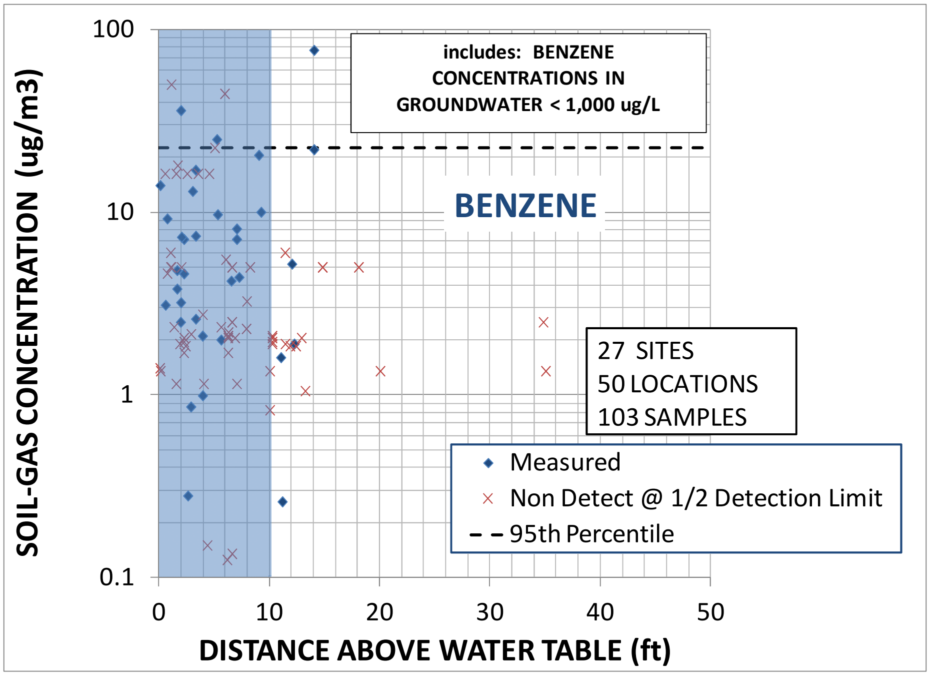

Figure 1. Benzene concentrations in soil gas as a function of distance above the water table for concentrations in groundwater < 1,000 µg/L. Analysis is based on soil gas data from Davis (2009) and Wright (2011).

Figure 2 - Lahvis (written communication)

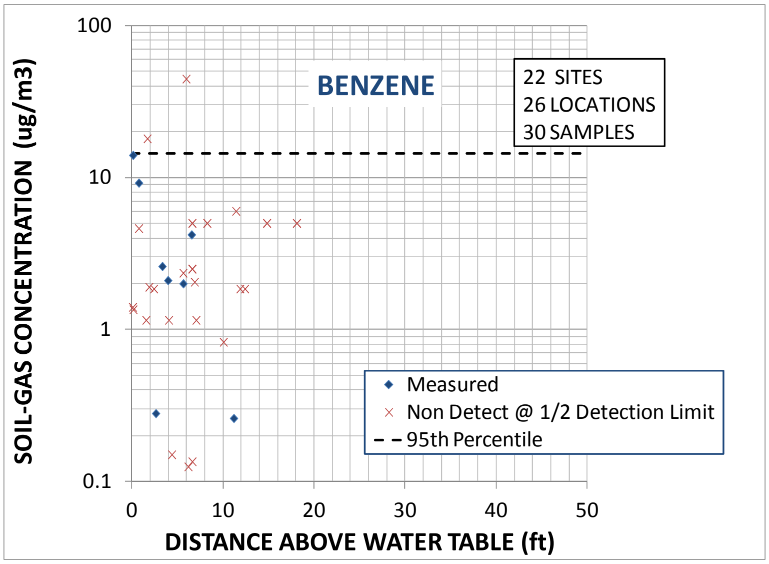

Figure 2. Benzene concentrations in soil gas as a function of distance above the water table for concentrations in groundwater < 100 µg/L. Analysis is based on soil gas data from Davis (2009) and Wright (2011).

- The probability of benzene vapor concentrations near the receptor exceeding a conservative screening level of 50 µg/m^3 is less than 5% at petroleum-UST release sites with benzene concentrations in groundwater < 1,000 µg/L. The probability is less than 5% regardless of the source-receptor separation distance (see Figure 3 – Lahvis [written communication]). The water table would have to be essentially in contact with a building foundation to create a potential concern for vapor intrusion at low concentration sites.

Figure 3 from Lahvis (written communication)

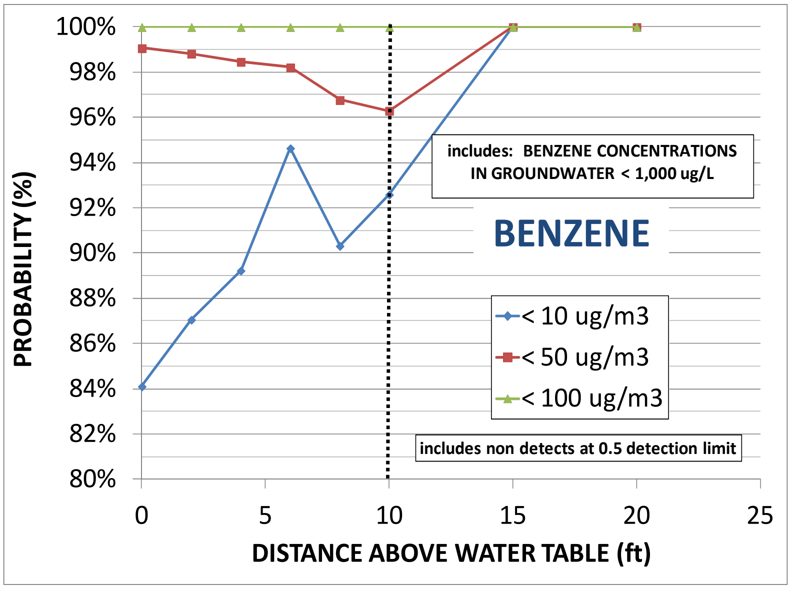

Figure 3. Probability of encountering benzene concentrations in soil gas above conservative screening-level concentrations of 10, 50, and 100 µg/m^3 at various distances above the water table at UST-only locations. The data are associated benzene (source) concentrations in groundwater < 1,000 µg/L and are taken from the databases reported in Davis (2009) and Wright (2011).

- The probability of benzene vapor concentrations near the receptor exceeding a (very) conservative screening level (i.e., 10 µg/m^3) at petroleum-UST release sites with benzene concentrations in groundwater < 100 µg/L is less than 5% regardless of the source-receptor separation distance (see Figure 4 from Lahvis [written communication]). The water table would have to essentially be in contact with a building foundation to create a potential concern for vapor intrusion at low concentration sites.

Figure 4 from Lahvis (written communication)

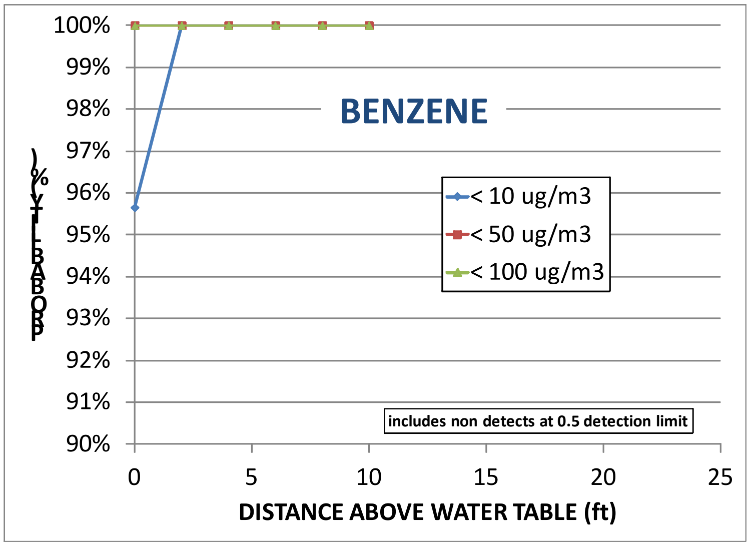

Figure 4. Probability of encountering benzene concentrations in soil gas above conservative screening-level concentrations of 10, 50, and 100 µg/m^3 at various distances above the water table at UST-only locations. The data are associated benzene (source) concentrations in groundwater < 100 µg/L and are taken from the databases reported in Davis (2009) and Wright (2011).

- The model results from Abreu et al. (2009) (see Figure 3 below) show O_2 concentrations in excess of ~17% (0.8 * 21%) for a hydrocarbon (benzene) vapor source concentration of 1 mg/L (1,000 µg/L) (see plots in middle of the figure). This benzene (or BTEX) vapor source concentration is roughly equivalent to a dissolved phase source concentration of ~4,000 µg/L, which is > the maximum dissolved-phase benzene concentration "1,000µg/L" defined for Scenario 3. This calculation assumes:

  a) the dissolved-phase source is primarily BTEX (the most soluble hydrocarbon fraction)
  b) vapor/aqueous partitioning occurs according to Henry's law, and
  c) a dimensionless Henry's Law partition coefficient for benzene (or BTEX) of 0.25.

- Analyses of soil-gas data from Davis (2010) and Wright (2011) show that O_2 concentrations in soil gas are > 4% (40,000 ppm_v) at sites with dissolved-phase sources of benzene in groundwater up to 15 mg/L (see Figure from Lahvis [2012]).

Figure 3 from Abreu et al (2009)

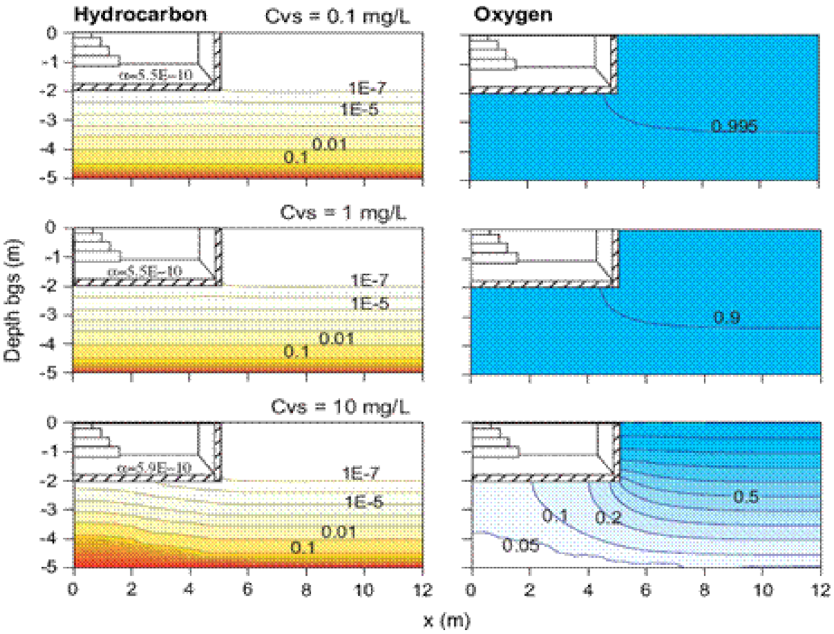

Figure 3. Effect of low vapor source concentration (Cvs) on soil-gas concentration distribution and vapor intrusion attenuation factors (α) for basement foundation scenarios and hydrocarbon biodegradation rate $\lambda = 0.79\ h^{-1}$. Hydrocarbon and oxygen concentrations are normalized by source and atmospheric concentrations, respectively.

Figure from Lahvis (2012)

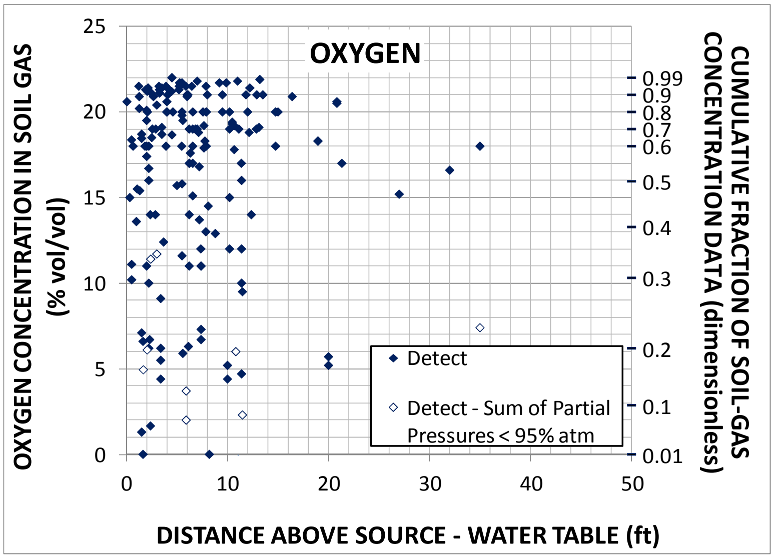

Figure. Plot of measured oxygen concentrations in soil gas as a function of distance above a dissolved-phase hydrocarbon source. Plot includes 192 soil-gas samples collected at 47 UST sites and 128 sampling locations. Non-detect data are omitted. Hollow points indicate selected data where the estimated sum of partial pressures in the sample is less than 95%. The cumulative fraction of all soil gas concentrations is noted on the right vertical axis. The oxygen concentrations are associated with dissolved-phase hydrocarbon (benzene) sources in groundwater with concentrations up to 15 mg/L Analysis is based on soil gas data from Davis (2009) and Wright (2011).

4.3 *Scenario 4: Direct Measurement of Soil Gas Concentrations*

Application of a thousand-fold attenuation factor to risk-based soil-gas criteria (i.e. CHSSLs) for sources located more than 5 vertical feet from a building foundation.

- Model results (see Figure 10 from Abreu et al., 2009) show that biodegradation produces an approximate 10,000-fold attenuation of benzene concentrations in soil-gas up to ~10 mg/L or 10,000,000 µg/m^3 within 2 m (5 ft) of a building foundation for reasonable approximations of the degradation rate in a sand unsaturated zone[12]. The proposed 1,000-fold additional attenuation for benzene concentrations in soil gas up to 85,000 and 280,000 µg/m^3 located more than vertical 5 feet from a building foundation is thus deemed conservative for residential and commercial settings, respectively.

Modified Figure 10 from Abreu et al. (2009)

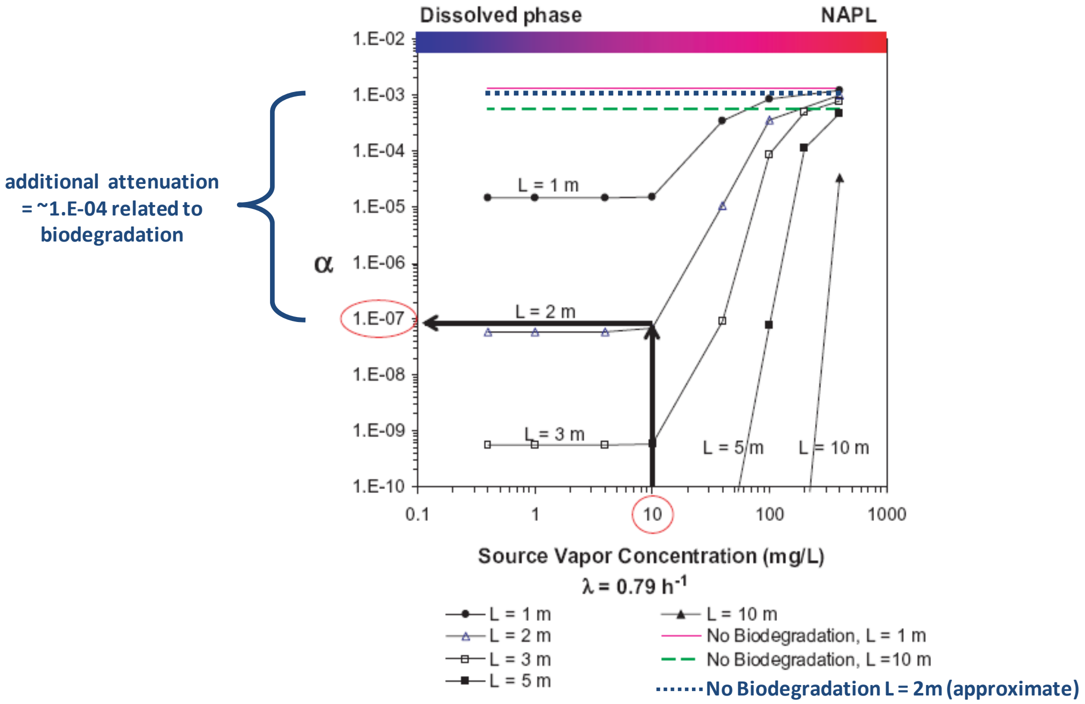

Figure 10. Use of the chart to select a semi-site-specific attenuation factor. For a source concentration of 10,000 µg/L and a source-building separation of 2 m, the attenuation factor would be about 1E-7.

- Measured field soil-gas (benzene) concentrations from Davis (2009) and Wright (2011) collected from vertically nested vapor probes support the model theory (see Figure below

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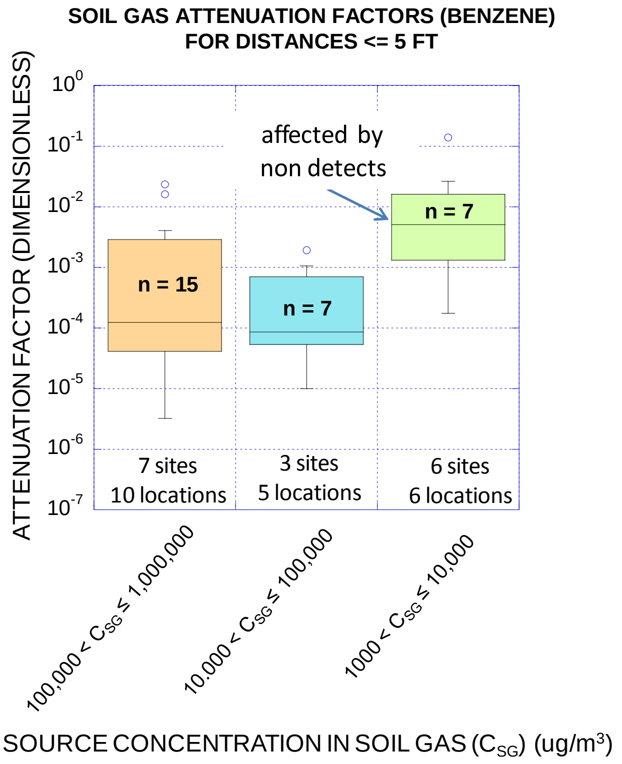
[12] Figure modified to show 'No Biodegradation L = 2m (approximate)' and additional attenuation to highlight technical justification.

from Lahvis [written communication]). More specifically, these data show that benzene attenuation in the unsaturated zone generally exceeds 1000-fold within a 5 feet vertical distance of a benzene (source) soil-gas concentration range between 10,000 and 100,000 µg/m^3 (see Figure 5 – middle box). Similar attenuation is observed for benzene soil gas (source) concentrations ranging between 100,000 and 1,000,000 µg/m^3 (see Figure 5 – left hand box). Less attenuation is observed for benzene soil gas (source) concentrations ranging between 1,000 and 10,000 µg/m^3 (see Figure 5 – right hand box). The statistics for this concentration range are affected, however, by non-detect values reported at ½ the detection limit. The soil-gas data are from the databases described by Davis (2009) and Wright (2011) for petroleum-UST release locations. This finding supports the model theory of Abreu et al. (2009) and the proposed use of a 1000-fold soil-gas bioattenuation factor.

Figure from Lahvis (written communication)



Each box encloses 50% of the data with the median value of the variable displayed as a line. The top and bottom of the box mark the limits of ± 25% of the variable population. The lines extending from the top and bottom of each box mark the minimum and maximum values within the data set that fall within an acceptable range defined by the software. Any value outside of this range, called an outlier, is displayed as an individual point.

Figure **5.** Box plots based on statistical analysis of benzene soil-gas data collected concurrently from vertically nested probe locations separated by distances ≤ 5 ft. The soil-gas data are taken from the databases reported in Davis (2009) and Wright (2011).

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CALIFORNIA LUFT MANUAL

APPENDIX B

SOIL BORING DESCRIPTION

Appendix B

Soil Boring Description

September 2012

This appendix provides guidance additional to that discussed in the Manual regarding proper logging of a soil boring.

Minimum Background for Well-Site Geologists

The well-site geologist should have a practical understanding of mass-wasting, soil-formation, and depositional processes sufficient to predict the likely subsurface geology based on the site setting. The geologist should be able to interpret geomorphology from local topography, comprehend relevant technical literature, and correlate drilling and hydrographic results from nearby sites. If the geologist lacks specific academic training, numerous practical references are available; examples include Fetter 2000, Rahn 1996, Miller and Donahue 1990, Reading (ed.) 1978, Blatt, Middleton, and Murray (1980), LeRoy and LeRoy (ed.) 1987, and Tearpock and Bischke 1991. The geologist should also have current HAZWOPER training and familiarity with drilling methods.

Project managers should require well-site geologists to write drilling prognoses prior to each phase of investigation. Prognoses should, at a minimum, include: total depth of investigation; depths to free seepage and refusal as appropriate; depths, thicknesses, and hydraulic conditions of permeable units; target sampling intervals; and potential mechanical and chemical health and safety issues.

Core Handling and Preservation

The driller should provide an appropriate working area, with a direct line of sight to the drilling crew, and appropriate support personnel and tools to assemble, disassemble, and decontaminate samplers and assist with core handling.

The well-site geologist should at minimum have the following equipment:

- Personal protective equipment
- Site safety plan
- Core record, logging, and monitoring well as-built forms
- Pollutant field-screening equipment, e.g., calibrated PID
- Appropriate soil and groundwater sampling equipment, e.g., soil sampling supplies, coolers, coolant, packing material, and disposable bailers
- Water level indicator
- Soil knives
- Weighted fiberglass measuring tapes
- Appropriate core storage, i.e., boxes and dividers
- Coring run labels
- Hand lens
- Munsell soil color charts
- Grain texture and composition estimation charts
- Dropper bottle with dilute hydrochloric acid (HCl)
- Graduated flask
- Squirt bottle
- Digital camera

- Appropriate core flags, e.g., colored toothpicks
- Wide, clear, adhesive tape
- Permanent markers
- Ice-cube tray

During drilling, the well-site geologist should focus on maintaining depth-accurate core recovery, preserving the core, and recording gross lithology changes and related drilling breaks. Other duties often include field screening for pollutants, sampling soils for potential laboratory analyses, monitoring for seepage, observing drill rig behavior, assisting with sampler decontamination, tracking investigation-derived wastes, and controlling drilling area access. During typical shallow borings with short trip-out times after each sample, insufficient time exists during drilling to focus on detailed logging.

Prior to drilling, the geologist should set up core boxes and dividers, marking dividers with arrows pointing up-core. To avoid storing cores upside-down, the geologist *must* communicate desired core orientation clearly to support crew. During drilling, the well-site geologist should gather preliminary information while the core is in the barrel, direct sample collection and transfer of cores into storage, label coring runs, and record information on a Core Record Sheet; see Table B-1, a partial form. Actual forms would call for further information—typically in the header or footer; for example, project name, date, time, location, drilling method and contractor, and geologist.

Table B-1: Example Core Record Sheet

Coring Run	Depth Penetrated (feet)	Feet Cut	Feet Recovered	Feet Not Recovered	PID Reading (ppmv)	Sample Number	Moisture	Lithology	Remarks
1	0 to 3.4	3.4	1.2	2.2	60, bottom of run	nnnn, 0.9 to 1.2, 10:30	dry	Asphalt 0.5 Fill	Bottle-cap in fill
2	3.4 to 8.4	5.0	3.4	1.6	70, bottom of run	nnnn, 6.3 to 6.8, 10:35	Slightly moist	CL 6.2 ML	Driller added sand catcher after Run #2
3	8.4 to 13.6	5.0	4.5	0.7; see remarks.	15, bottom of run	nnnn, 8.6 to 8.9 11:00	Slightly moist	ML 8.9 SM	Muscovite[1] Driller extended shoe 0.2' beyond run
4	13.6 to 18.6	5.0	5.0	0	200, at contact, SP/CL	nnnn, 18.2 to 18.5, 11:15	Moist Very Moist	SM 14.2 SP CL 18.2	Bedforms[2] Bedforms[2] Slight fuel odor

Notes:

CL	Clay
ML	Silt
nnnn	Example of sample number
ppmv	Part per million vapor
SM	Silty sand
SP	Poorly graded sand

1) Abundant muscovite in silt, 8.6 to 8.9
2) Bedforms, Run #4, in SM, 13.6 to 14.2, even parallel, continuous, laminae, 1 to 5 mm, sharp, with heavy mineral segregation. Also in SP, 16.5 to 17.2, uneven, nonparallel, discontinuous, faint, in sets about 2 to 5 cm, photographs taken, co-sets marked in frames.

In the example above, it is important to note that *Coring Run*, *Depth Penetrated*, *Feet Cut*, and *Feet Not Recovered* are depths penetrated relative to grade surface. The depths are measured, precise to the nearest 1/10 foot (~ 1 inch). For maps and cross sections, in normal drilling environments, for example HSA in alluvium, one can usually later assume depth-accuracy to within about ½ foot.

The geologist should mark a corresponding core label with information in the first four columns, and place it in core storage at the bottom of each run. While no-recovery intervals are usually at the tops of core barrels, most geologists typically assume footage not recovered is from the bottoms of coring runs. This is generally correct, but exceptions can occur, for example, due to a partially obstructed sampler shoe, slough, and heaving sands. To avoid inaccuracies, the geologist should communicate closely with the driller.

Note also the columns titled *PID Reading*, *Sample Number*, and *Moisture*. On Coring Run #4, the PID reading and sample are from a specific geologic contact, and reflect a judgmental sample. Notes in the *Moisture* column reflect conditions during drilling.

Columns titled *Lithology* and *Remarks* are key to accurate core description. The well-site geologist should fill these in prior to removing the core from the barrel. Dashed lines in the *Lithology* column depict gradational contacts; solid lines, sharp contacts. The contact at 18.2 feet below ground surface (bgs), a wavy solid line, is a scour surface. To avoid inaccurate measurements, the well-site geologist should scrape the core with a soil knife to get through zones affected by frictional smearing. Notes in the *Remarks* column in this case show evidence of fill, drilling actions, and, importantly, sedimentary structures likely to be disturbed during removal of the core from the barrel. For example, on Core Run #4, see especially the remark "bedforms," and related Footnote 2.

Sedimentary structures and textures are difficult to preserve while transferring the core into ambient storage. To keep pace with the driller, the well-site geologist must develop techniques to quickly describe the core in the barrel. For example, one can apply a strip of clear adhesive tape to sands, annotating features with a waterproof marker, retaining the strip for later detailed logging. To describe graded beds, one can collect sub-samples at discrete depths, for example into an ice-cube tray. For bedforms (e.g., laminae, ripples, cross-bedding, etc.), the McKee and Weir (1953) classification system is recommended. One can also digitally photograph the core, marking key features with appropriate core flags.

Follow-Up Detailed Logging

All logged intervals should at minimum begin with ASTM/USCS Group Symbols and Group Names, followed by Munsell Colors (hue, value, and chroma codes). For fine-grained soils, ≥50% finer than #200 sieve, descriptions should, at a minimum, continue with plasticity, toughness, and dilatancy. As appropriate, descriptions should also include reaction with HCl, *soil* (pedogenic) structures, cementation, root bores, and accessory minerals. For silts, Group Symbol ML, especially those with Group Names *Silt with Sand* and *Sandy Silt*, log appropriate *sedimentary* structures.

For coarse-grained soils (sediments), <50% finer than #200 sieve, descriptions should continue with texture, composition, and sedimentary structures. Texture should generally include total size range and modes, in millimeters (mm), grain shape, using the Powers (1953) chart for sands, USCS/ASTM for gravels, and estimated sorting. Efficient estimates of grain size distributions are feasible in the field; we suggest conducting water-settling tests in a graduated cylinder. Textural descriptions should be sufficient to describe vertical grading within permeable units (e.g., fining- and coarsening-upward sequences).

Composition should include hand-lens estimated percentages of quartz, feldspars, and rock fragments, normalized for sand and larger particles. Composition should also include accessory minerals (e.g., heavy minerals and muscovite) and fossils. For gravels, descriptions should be reasonable based on hand lens description, but sufficient to correlate to local outcrops at basin margins. For example, "granitoid with modal sodic feldspar and dark minerals" would be reasonable; further details, such as specific mineralogy, would be questionable based solely on a hand lens description.

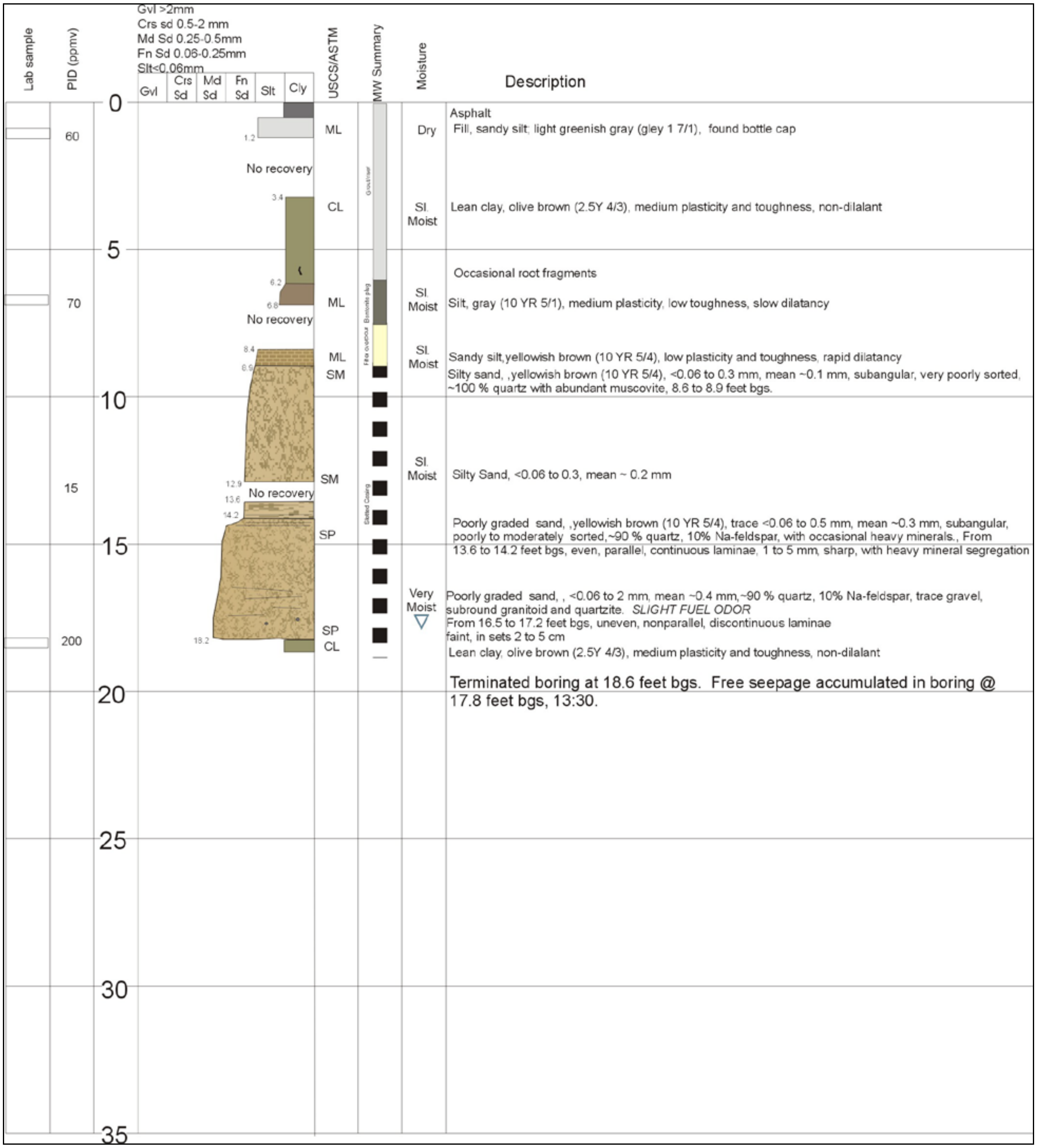
Sedimentary structures are bedding, bedforms, soft sediment deformation features, and trace fossils. Bedding descriptions should generally include thicknesses of sets and co-sets. Descriptions of bedforms should be sufficient to allow reasonable estimates of depositional flow velocities. Soft sediment deformation features, such as load casts and convoluted bedding, occasionally found in core, can provide evidence of rapid burial of an under-compacted substrate. Trace fossils, for example escape burrows and feeding traces, can likewise indicate burial history.

Descriptions of coarse-grained intervals, based on texture, composition, and sedimentary structures, should in general be sufficient to allow reasonable interpretation of depositional environment (e.g., alluvial fan, braided stream, point bar, estuary, beach, etc.).

All descriptions should end with, or otherwise emphasize, field moisture content and evidence of pollution. Evidence of pollution, staining, odor, and sheen, should appear in italics.

Various formats exist for boring logs. Most useful formats show on each page: the graphics of permeable units, monitoring-well construction summaries, and first free seepage observed while drilling. Figure B-1 is an example log, based on the above core record sheet. This is a partial form; typical header information, which has been omitted, includes project name, location, date, time, drilling and sampling methods, contractor, geologist, surface elevation, etc. Also note that detailed monitoring well as-builts should accompany logs.

Figure B-1: Example of a Boring Log



Asphalt
Fill, sandy silt; light greenish gray (gley 1 7/1), found bottle cap

Lean clay, olive brown (2.5Y 4/3), medium plasticity and toughness, non-dilalant

Occasional root fragments

Silt, gray (10 YR 5/1), medium plasticity, low toughness, slow dilatancy

Sandy silt,yellowish brown (10 YR 5/4), low plasticity and toughness, rapid dilatancy

Silty sand, ,yellowish brown (10 YR 5/4), <0.06 to 0.3 mm, mean ~0.1 mm, subangular, very poorly sorted, ~100 % quartz with abundant muscovite, 8.6 to 8.9 feet bgs.

Silty Sand, <0.06 to 0.3, mean ~ 0.2 mm

Poorly graded sand, ,yellowish brown (10 YR 5/4), trace <0.06 to 0.5 mm, mean ~0.3 mm, subangular, poorly to moderately sorted,~90 % quartz, 10% Na-feldspar, with occasional heavy minerals., From 13.6 to 14.2 feet bgs, even, parallel, continuous laminae, 1 to 5 mm, sharp, with heavy mineral segregation

Poorly graded sand, , <0.06 to 2 mm, mean ~0.4 mm,~90 % quartz, 10% Na-feldspar, trace gravel, subround granitoid and quartzite. *SLIGHT FUEL ODOR*
From 16.5 to 17.2 feet bgs, uneven, nonparallel, discontinuous laminae
faint, in sets 2 to 5 cm

Lean clay, olive brown (2.5Y 4/3), medium plasticity and toughness, non-dilalant

Terminated boring at 18.6 feet bgs. Free seepage accumulated in boring @ 17.8 feet bgs, 13:30.

The above log indicates a point bar, a commonly encountered sand deposit, from about 6.8 to 18.2 feet bgs. Top of the deposit is an inference based on a lost core, assumed to have fallen from the barrel due to lack of cohesion. Based on depth to free seepage, the sand is likely hydraulically unconfined. Because the slotted casing interval extends nearly to the top of the sand, and the water table might rise, slotted casing and filter media choice should account for the finest-grained portion of the deposit.

Assuming the point bar is 11.4 feet thick (h), roughly similar to bank-full channel depth, and the channel is highly sinuous, the approximate width (w) of the sand body in the subsurface is ($w = 6.8h^{1.54}$), or around 290 feet (Leeder 1973). Its shape is likely lunate, roughly a half-moon. Because gravels near the base of the deposit include granitoid rocks, one could assume the deposit came from an intrusive igneous source, which could narrow the search direction for the edge of the sand. At the convex margin of the sand, one might expect an oxbow plug, a fat clay that could greatly affect remedial system performance.

An experienced, adequately trained well-site geologist can typically generate a description similar to the above in about one hour. Description heavily relies on proper core handling and preservation.

CALIFORNIA LUFT MANUAL

APPENDIX C

VAPOR INTRUSION

Appendix C
Vapor Intrusion
September 2012

This appendix discusses the Vapor Intrusion (VI) pathway for petroleum hydrocarbons at leaking underground fuel tank (LUFT) sites.

Warning! The assessment methodologies described herein may not be appropriate to address conditions of immediate concern such as explosion hazard or acute health impacts. If petroleum hydrocarbon odors are reported for a structure, or if field screening indicates volatile organic compound (VOC) concentrations where flammability concerns are raised (e.g., concentrations greater than 25% lower explosive limit [LEL]), then prompt action to protect the building and occupants should be taken.

Vapor intrusion (VI) is the term used to describe the migration of VOCs from sub-surface soil and/or groundwater upward, via soil vapor, into buildings, potentially causing an unacceptable chemical exposure for building occupants (State of California Department of Toxic Substances Control [DTSC] 2011a).

When a petroleum release occurs at a LUFT site, petroleum is typically released as a light non-aqueous-phase liquid (LNAPL). LNAPL moves vertically downward through the unsaturated zone in response to gravity and capillary forces until either a relatively impermeable zone or the water table is encountered. Several factors, including the volume of the release, rate of the release, hydraulic conductivity of the soils, depth to the water table, and adsorptive capacity of the subsurface materials, will determine whether LNAPL will ultimately migrate downward to the area of the capillary fringe and the water table or will remain entirely in the vadose zone. As partitioning from liquid to vapor phase takes place, vapors migrate vertically (upward) toward the ground's surface. The migration of the contaminants may pose a threat to occupants living or working above the source of contamination.

Background

The potential adverse effects to human health by VI due to VOCs in soil, groundwater, and soil vapor garnered significant attention from regulatory agencies in the late 1990s. Over the past decade many agencies, including the U.S. Environmental Protection Agency (EPA), DTSC, the California Regional Water Quality Control Boards (Regional Water Boards), state and local regulatory agencies have developed policy or guidance on how to address the issue of VI.

In May 2012, the State Water Resources Control Board (State Water Board) adopted Resolution 2012-0016, Low-Threat Underground Storage Tank (UST) Case Closure Policy (Case Closure Policy), effective August 17, 2012 (State Water Board, 2012a). It contains criteria that may exclude petroleum sites from VI assessments. These criteria will be covered later in this Appendix.

The DTSC and the North Coast, Los Angeles, and San Francisco Regional Water Boards have each developed guidance documents that address VI in varying degrees. Most of these guidance documents are generally based in part on the California DTSC guidance. The North Coast Regional Water Board and the DTSC provide comprehensive guidance documents for assessing the potential of VI. It is important to note that these guidance documents address all types of contamination, not just contamination from petroleum USTs (North Coast Regional Water Board 2009).

History. The following are significant guidance documents or events that represent milestones in VI development and understanding. Note that these documents primarily address chlorinated hydrocarbon compounds and may not be ideal or all-inclusive of petroleum sites where biodegradation is present. In late 2012, vapor-intrusion guidance from the EPA Office of Underground Storage Tanks (OUST) is expected to be released for petroleum hydrocarbon sites. In 2013, the Interstate Technology and Regulatory Council (ITRC) is expected to release additional guidance on VI of petroleum-related hydrocarbons.

2002 – EPA Office of Solid Waste and Emergency Response (OSWER) – Vapor Intrusion Guidance
2003 – DTSC Soil Gas Sampling Advisory (Guidance) – Updated in April 2012
2004/2005 – DTSC VI Guidance Document – Updated in October 2011
2007 – Interstate Technology & Regulatory Council (ITRC) VI Practical Guideline
2007 – ITRC VI Scenario Document
2007/2008 – American Society for Testing and Materials (ASTM) VI Standard Practice
2011 – EPA Information Paper regarding Petroleum VI versus Chlorinated VI
2012 – California State Water Board Low-Threat UST Case Closure Policy (Resolution 2012-0016)

Conceptual Site Model

The VI pathway evaluation should be conducted in a manner consistent with the Conceptual Site Model (CSM) chapter. The CSM describes the contaminant sources, transport/exposure pathways, and potential receptors for the site. In order for the VI pathway to be complete, each of these CSM components must be present and connected. If a petroleum source is not present, or a continuous exposure pathway from the source to the receptor is not present, then the pathway can be eliminated from further consideration. Additionally, if conditions meet the criteria of the Case Closure Policy, the pathway may also be eliminated from further consideration. However, any future changes to the site use could trigger a re-evaluation of the VI pathway.

The conceptual model for the VI pathway for petroleum hydrocarbons includes the following potential fate-and-transport mechanisms:

- Volatilization of constituents from soil or groundwater to soil gas;
- Diffusion of the constituents in soil gas through the vadose zone;
- Biodegradation of the constituents within portions of the vadose zone with sufficient oxygen to promote aerobic biodegradation;
- Convection of soil gas to indoor air through cracks and/or openings in the building foundations;
- Convection of soil gas to outdoor air;
- Ambient air concentrations; and
- Mixing of the constituents within the structure due to building ventilation.

Source characteristics considered in the conceptual model for VI for LUFT sites include the following:

- Identification of constituents of concern (COCs);
- Concentrations of the COCs in the impacted media; and
- Lateral and vertical distances between the bottom of the building and the impacted soil, groundwater or product (e.g., is the soil beneath the building impacted or not?).

Pathway characteristics considered in the VI conceptual model include the following and are further discussed in the Evaluation of Complete Vapor Migration Pathway section below:

- Soil properties affecting diffusion of constituents through the vadose zone (e.g., soil type, total porosity, and water-filled porosity);
- Evidence of zones favorable for aerobic biodegradation (i.e., presence of oxygen in the subsurface);

- Building characteristics (commercial/residential building, vertical and lateral distances from the top of the contamination to the floor inside the building , type of building foundation, the thickness of the building foundation, the thickness of the building foundation that is buried below grade, details about the presence of cracks, whether the building has a basement or not);
- Surface cover at site (asphalt, concrete, soil, grass);
- Building ventilation properties that may affect convection of soil gas into the structure (e.g., positively pressurized building, ventilation air-exchange rate), and mixing in the building; and
- Corrective measures in place that may limit migration of constituents into the building (e.g., source remediation, mitigation measures such as a vapor barrier).

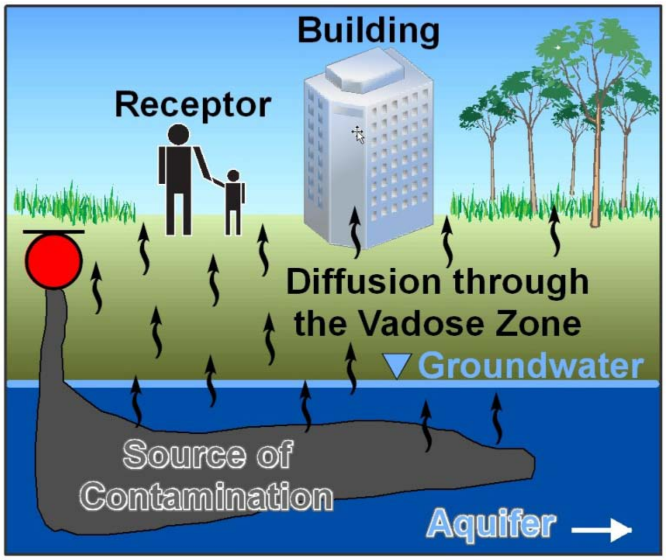
Receptor characteristics considered in the VI conceptual model include the following:

- Building occupant type (e.g., commercial, residential);
- Age of occupants (e.g., children, adults); and
- Existing or potential future buildings.

Exposure assumptions or characteristics considered in the VI conceptual model include the following:

- Daily time frame (e.g., 8 hours per day, 24 hours per day); and
- Duration (e.g., 30 years for residences, 25 years for commercial)

Figure C-1: Source, Pathway, Receptor



Evaluation of Complete Vapor Migration Pathway

In order to assess the potential risks of VI into surrounding buildings, it is important to identify whether the vapor migration pathway is complete. VI pathway assessments for petroleum hydrocarbon sites differ from evaluations for chlorinated VOC sites, because petroleum hydrocarbons can readily degrade under aerobic conditions in the vadose zone. Soil microbes which degrade petroleum-based hydrocarbons are ubiquitous in soil. Under the appropriate conditions (Scenarios 1 through 4 of the Case Closure Policy), the rate of biodegradation in the vadose zone may be sufficient to cause the vapor migration pathway to be incomplete (State Water Board 2012b; Davis 2009). These conditions include:

- Adequate oxygen in the soil ;
- Clean soil (total petroleum hydrocarbons [TPH] <100 milligrams per kilogram [mg/kg]) between the contamination and the affected building; and
- Low dissolved levels of contamination in groundwater-specific conditions to cause the vapor migration pathway to be incomplete are discussed below in the Pathway Screening Section.

It is important to note that there are other site characteristics which could cause the pathway to be incomplete, such as VOCs not volatilizing from groundwater, or lithology inhibiting soil-vapor migration upwards. A site assessment including soil-gas sampling for the presence of oxygen and carbon dioxide (a by-product of the biodegradation process) is useful to properly ascertain whether sufficient biodegradation of petroleum vapors is likely to be occurring in the vadose zone. Soil-phase concentration data are also required in the Case Closure Policy to confirm the presence of clean soil.

Preferential Pathways

When evaluating whether the vapor migration pathway is complete, it is important to consider preferential pathways, physical site conditions that can be an avenue for soil-vapor migration. These avenues may complete the vapor migration pathway, even when the pathway screening criteria appear to be satisfied. Examples of preferential pathways:

- Large underground utility trenches (storm drains)
- Fractured bedrock
- Basement sumps
- Elevator shafts
- Large utility vaults

If a source of VOCs, migration/transport pathways, and receptor and exposure pathways all exist, then the VI pathway may need to be assessed at a LUFT site.

Biodegradation of Petroleum Hydrocarbons

As discussed in the Fate and Transport chapter of this Manual, petroleum hydrocarbons naturally biodegrade under both aerobic and anaerobic conditions. The simplest, most water-soluble constituents are biodegraded first (e.g., benzene, toluene, ethylbenzene xylene [BTEX], and the small *n*-alkanes); the more complex molecular structures are biodegraded more slowly.

Bacteria ubiquitous in the environment cause the biodegradation. These bacteria are important in the natural attenuation of dissolved hydrocarbons, serving to limit the migration of VOCs in groundwater. The bacteria are equally effective in the vadose zone. A number of field studies have documented the biodegradation of petroleum constituents in the vadose zone (e.g., Davis, et al. 2009; American Petroleum Institute [API] 2001; Pasteris, et al. 2002; Lundegard and Johnson 2006; Davis 2006). DeVaull, in his 2007 publication, *Indoor Vapor Intrusion with Oxygen-Limited Biodegradation for a Subsurface Gasoline Source,* compiled aerobic hydrocarbon biodegradation rates in vadose-zone pore-water from numerous studies. Although the reported degradation rates varied between studies, within the gasoline range (i.e., C6 to C12 hydrocarbons), the only clear difference by hydrocarbon class was between aromatic and aliphatic hydrocarbons. DeVaull reported a geometric mean degradation rate of 0.79/hour for aromatic hydrocarbons (based on 84 data sets) and 71/hour for aliphatic hydrocarbons (straight chain and branched, based on 17 data sets). These groups do not include fuel additives such as methyl tert butyl ether (MTBE).

Several model studies of petroleum VI that account for aerobic biodegradation have evaluated the combined impact of oxygen demand and degradation rate on petroleum VI (Parker 2003; Abreu and Johnson 2006; DeVault 2007; Abreu, et al. 2009). For the evaluations conducted by Abreu, et al. (2009), petroleum vapor attenuation was not oxygen-limited for vapor source concentrations less than 10,000,000 micrograms per cubic meter (µg/m^3) or 10 milligrams per liter (mg/L). In the cases where attenuation was not oxygen-limited, the distance required between the building foundation and the dissolved petroleum source to ensure high petroleum VOC attenuation depended on the first-order degradation rate. When using the geometric mean biodegradation rate for aromatic hydrocarbons (0.79/hour), a separation distance between the source and the building of 1 m (3 ft) was sufficient to achieve 100x bioattenuation (i.e., a 100x increase in attenuation relative to the “no biodegradation” case), while a separation distance of 3 m (10 ft) resulted in 10,000x bioattenuation. When using the lower degradation rate (0.079/hour), a separation distance of 3 m (10 ft) was required to achieve 100x bioattenuation.

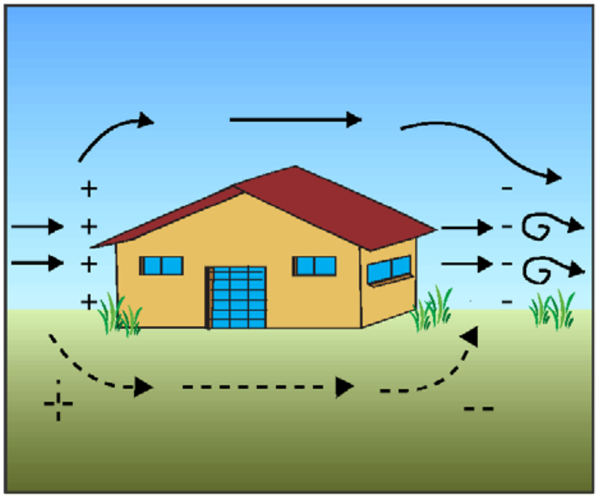
The modeling conducted by DeVaull (2007) indicates a similar range of bioattenuation. Based on the range of aerobic diffusion reaction lengths (i.e., the distance over which the concentration is reduced by 50%) reported for benzene (2.3 to 29 centimeters [cm]), the bioattenuation expected to occur over a distance of 3 m is at least 1000x (API 2009).

The available scientific literature related to petroleum vapor fate, transport, and intrusion into buildings suggests that aerobic biodegradation can serve as a barrier to petroleum VI at sites with sufficient separation between the source and the building foundation.

Oxygen Transport below Buildings

A number of mechanisms have been identified that can transport oxygen from the atmosphere into the subsurface below a building foundation. For example, when wind strikes a building, a pressure gradient is created, with higher pressure on the upwind side and lower pressure on the downwind side of the building, as shown in the figure below. This pressure gradient can result in advection of atmospheric air though the soil below the building, transporting oxygen from the atmosphere into the shallow soil gas, thereby allowing for aerobic biodegradation (Lundegard, et al. 2008, Fischer, et al. 1996).

Figure C-2: Pressure Gradient Created by Windon a Building



Luo and others present soil-gas concentration profiles for TPH and oxygen under the footprint of a building overlying petroleum hydrocarbon-impacted soils. These data indicate a spatial correlation between the dominant wind direction and concurrent low concentrations of TPH and high concentrations of oxygen (Luo, et al. 2009).

In addition to wind-driven oxygen transport, in buildings with continuous or transient positive-pressure conditions, air will flow from the building to the shallow soils through any foundation cracks or other penetrations, providing an additional source of oxygen below the foundation (McHugh, et al. 2006). Many commercial buildings are maintained at a positive pressure relative to the atmosphere by the heating, ventilation, and air-conditioning (HVAC) system, and passively ventilated buildings (e.g., typical single-family residences) typically fluctuate between positive and negative pressure due to wind effects and other transient conditions, such as barometric pressure fluctuations.

Pathway Screening

The objective of a VI pathway screening is to evaluate whether the site requires further action, such as additional sampling or mitigation.

There are a number of criteria to be considered when evaluating a site for VI. At a minimum, LUFT sites should be investigated so they can be compared to criteria in the Case Closure Policy. The Case Closure Policy's VI scenarios are illustrated below; its numerical criteria are included on tables in Figures C-7 and C-8. Table C-3 may also be used as a screening tool for sites that do not fit the Case Closure Policy criteria.

Scientific understanding of how vadose-zone biodegradation serves as a barrier to petroleum VI supports the pathway screening criteria presented in the following four scenarios and on tables in Figure C-7, Figure C-8, and Table C-3; however, care must be used in identifying preferential pathways or uncharacterized source areas that could cause VI impacts, even when the pathway screening criteria appear to be satisfied.

Vapor Intrusion Risk Screening Criteria from the Case Closure Policy

In the Low-Threat UST Case Closure Policy, a LUFT site is assumed to present no unacceptable risk from vapor intrusion if any of the following conditions exists:

1. Site-specific conditions satisfy all the characteristics/criteria of scenarios 1 through 3, or all characteristics/criteria of scenario 4 (see following);
2. A site-specific risk assessment for the VI pathway demonstrates that human health is protected; or
3. Use of mitigation measures or institutional/engineering controls reduces exposure, and no significant risk to human health exists.

The following summarizes the four scenarios where VI is considered low-threat and a site-specific VI assessment will not be required for a site. Graphical representation of each scenario is presented on Figures C-3 through C-8.

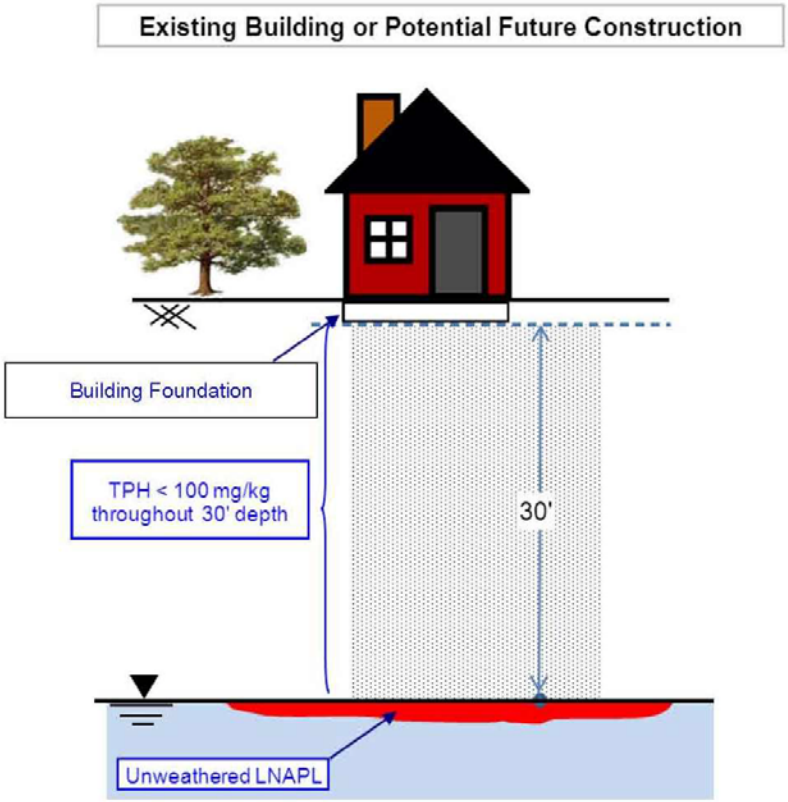
1. **Scenario 1:** *For measurable unweathered LNAPL in groundwater*. 30 feet or more of clean soil between the bottom of existing or future building's foundation and LNAPL in groundwater are required.
2. **Scenario 2:** *For soil with unweathered LNAPL*. 30 feet of vertical and lateral separation or more of clean soil between the bottom of existing or future building's foundation and LNAPL in soil are required.
3. **Scenario 3a:** *For low and high-strength groundwater sources and Bioattenuation Zone with No Oxygen Data or Oxygen <4%*. 1) 5 feet or more of clean soil between the bottom of existing or future building's foundation and the shallowest impacted groundwater with benzene concentration less than 100 micrograms per liter (µg/L); or 2) 10 feet or more of clean soil between the bottom of existing or future building's foundation and the shallowest impacted groundwater with benzene concentration greater than or equal to 100 µg/L and less than 1,000 µg/L.
4. **Scenario 3b:** *For high-strength groundwater sources and Bioattenuation Zone with Oxygen ≥ 4%*. 5 feet or more of clean soil between the bottom of existing or future building's foundation and the shallowest impacted groundwater with benzene concentration less than 1,000 µg/L; oxygen concentration in the vadose zone has been measured and is greater than or equal to 4%.
5. **Scenario 4a:** *For sites with soil gas data and no Bioattenuation Zone*. Collection of soil gas sample at least 5 feet below existing or future building's foundation; screening levels as shown on the table in Figure C-7 are required.
6. **Scenario 4b:** *For sites with soil gas data and Bioattenuation Zone*. Collection of soil gas sample at least 5 feet below existing or future building's foundation; oxygen concentration at lower end of the zone is greater than or equal to 4%; screening levels as shown on the table in Figure C-8 are required.

In the unsaturated (vadose) zone, "clean soil" is defined as soil containing TPH concentrations less than 100 mg/kg. Under these conditions, it is assumed that natural attenuation is sufficient to mitigate concentrations of volatile petroleum constituents. Conversely, if these conditions do not apply at a particular LUFT site, a site-specific VI risk evaluation may be required.

Justification for these distances can be found in Technical Justification for Vapor Intrusion Media-Specific Criteria (State Water Board, 2012b). It should be noted that some of the exclusion distances for the Case Closure Policy criteria are larger than those in many of the published studies on petroleum VI; this is because the State Water Board added a factor of safety for the Case Closure Policy.

FigureC-3: Scenario 1 – Unweathered* LNAPL in Groundwater

Required Characteristics of the Bioattenuation Zone



Required Characteristics of the Bioattenuation Zone:

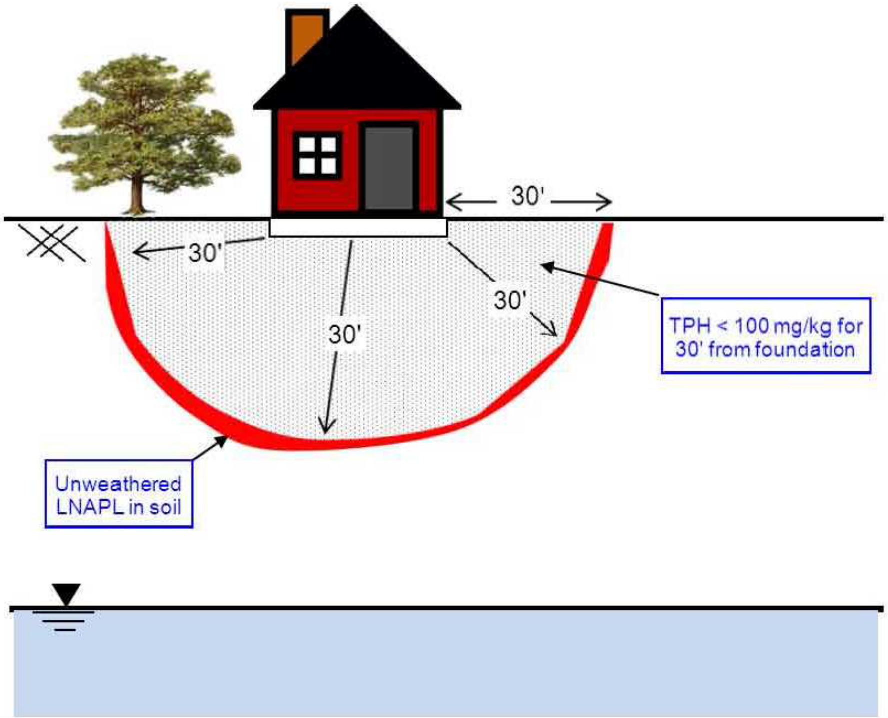
1. The bioattenuation zone shall be a continuous zone that provides a separation of at least 30 feet vertically between the LNAPL in groundwater and the foundation of existing or potential buildings; and
2. Total TPH (TPH-g and TPH-d combined) are less than 100 mg/kg throughout the entire depth of the bioattenuation zone.

TPH = total petroleum hydrocarbons
TPH-g = total petroleum hydrocarbons as gasoline
TPH-d = total petroleum hydrocarbons as diesel

*As used in this context, unweathered LNAPL is generally understood to mean petroleum product that has not been subjected to significant volatilization or solubilization, and therefore has not lost a significant portion of its volatile or soluble constituents (e.g., comparable to recently dispensed fuel).

Figure C-4: Scenario 2 – Unweathered* LNAPL in Soil

Required Characteristics of the Bioattenuation Zone



Existing Building or Potential Future Construction

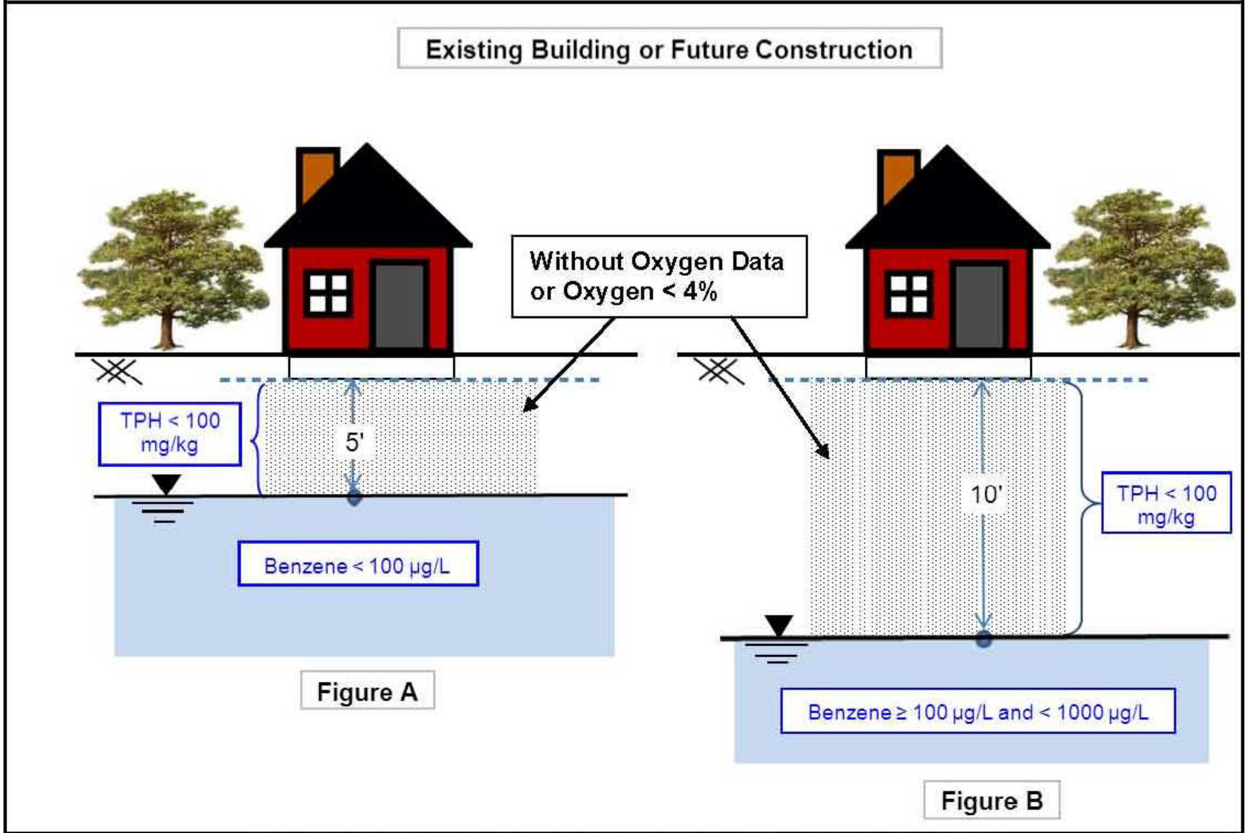
Required Characteristics of the Bioattenuation Zone:

1. The bioattenuation zone shall be a continuous zone that provides a separation of at least 30 feet both laterally and vertically between the LNAPL in soil and the foundation of existing or potential buildings, and
2. Total TPH (TPH-g and TPH-d combined) are less than 100 mg/kg throughout the entire lateral and vertical extent of the bioattenuation zone.

*As used in this context, unweathered LNAPL is generally understood to mean petroleum product that has not been subjected to significant volatilization or solubilization, and therefore has not lost a significant portion of its volatile or soluble constituents (e.g., comparable to recently dispensed fuel).

Figure C-5: Scenario 3a – Dissolved-Phase Benzene Concentrations in Groundwater (Low concentration groundwater scenarios with or without oxygen data)

Defining the Bioattenuation Zone Without Oxygen Data or Oxygen < 4%



Required Characteristics of Bioattenuation Zone for Sites Without Oxygen Data or Where Oxygen is < 4%

Figure A: 1) Where benzene concentrations are less than 100 µg/L, the bioattenuation zone:

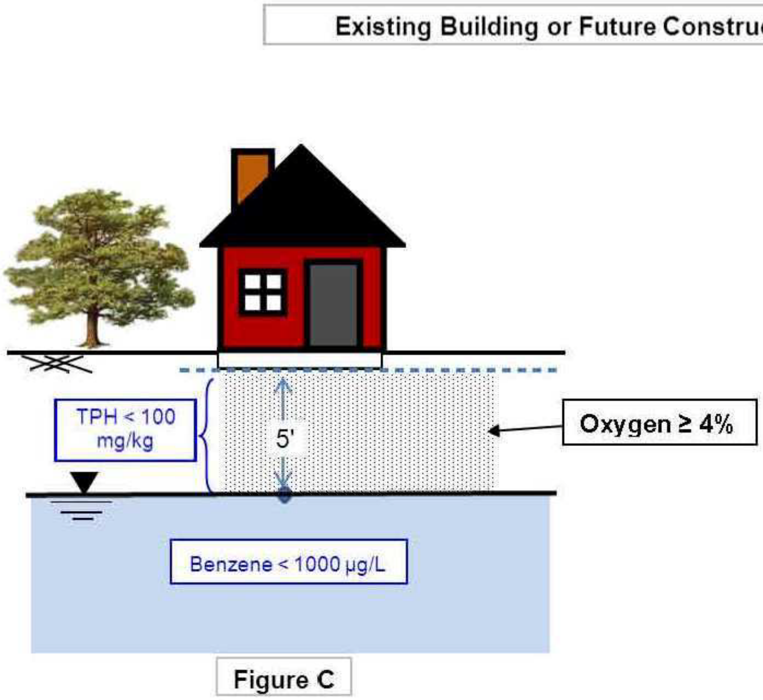
a) Shall be a continuous zone that provides a separation of at least 5 feet vertically between the dissolved phase Benzene and the foundation of existing or potential buildings; and
b) Contain Total TPH (TPH-g and TPH-d combined) less than 100 mg/kg throughout the entire depth of the bioattenuation zone.

Figure B: 1) Where benzene concentrations are equal to or greater than 100 µg/L but less than 1000 µg/L, the bioattenuation zone:

a) Shall be a continuous zone that provides a separation of at least 10 feet vertically between the dissolved phase Benzene and the foundation of existing or potential buildings; and b) Contain Total TPH (TPH-g and TPH-d combined) less than 100 mg/kg throughout the entire depth of the bioattenuation zone.

Figure C-6: Scenario 3b – Dissolved Phase Benzene Concentration in Groundwater (Low concentration groundwater scenarios with and without oxygen data)

Defining the Bioattenuation Zone With Oxygen ≥ 4%



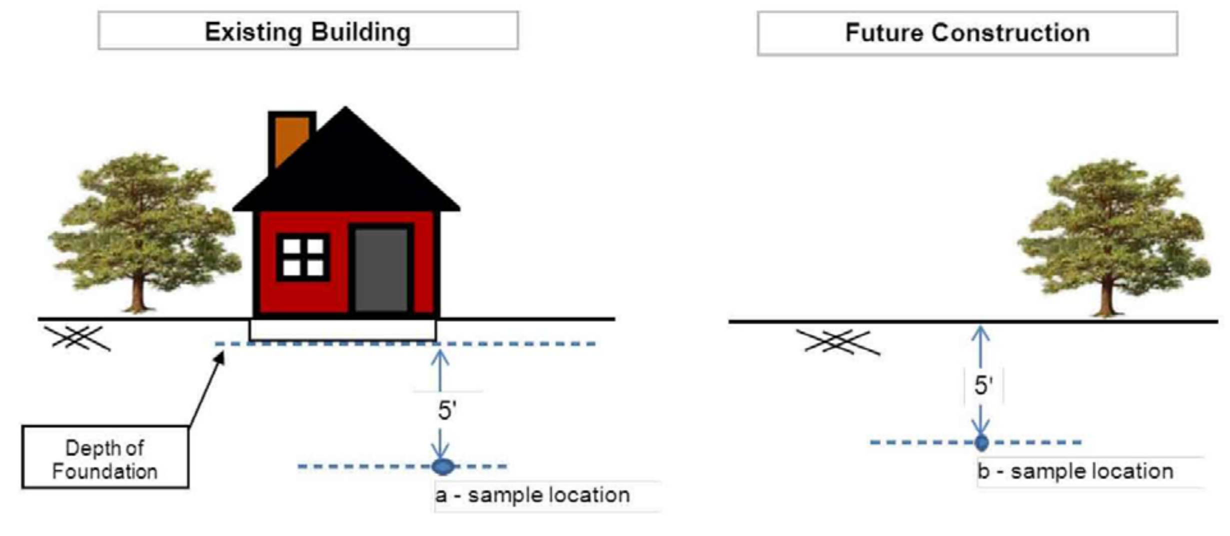
Required Characteristics of Bioattenuation Zone for Sites With Oxygen ≥ 4%

Where benzene concentrations are less than 1000 µg/L, the bioattenuation zone:

1. Shall be a continuous zone that provides a separation of least 5 feet vertically between the dissolved phase Benzene and the foundation of existing or potential buildings; and
2. Contain Total TPH (TPH-g and TPH-d combined) less than 100 mg/kg throughout the entire depth of the bioattenuation zone.

Figure C-7: Scenario 4a - Direct Measurement of Soil Gas Concentrations

Soil Gas Sampling – No Bioattenuation Zone



The criteria in the table below apply unless the requirements for a bioattenuation zone, established below, are satisfied.

When applying the criteria below, the soil gas sample must be obtained from the following locations:

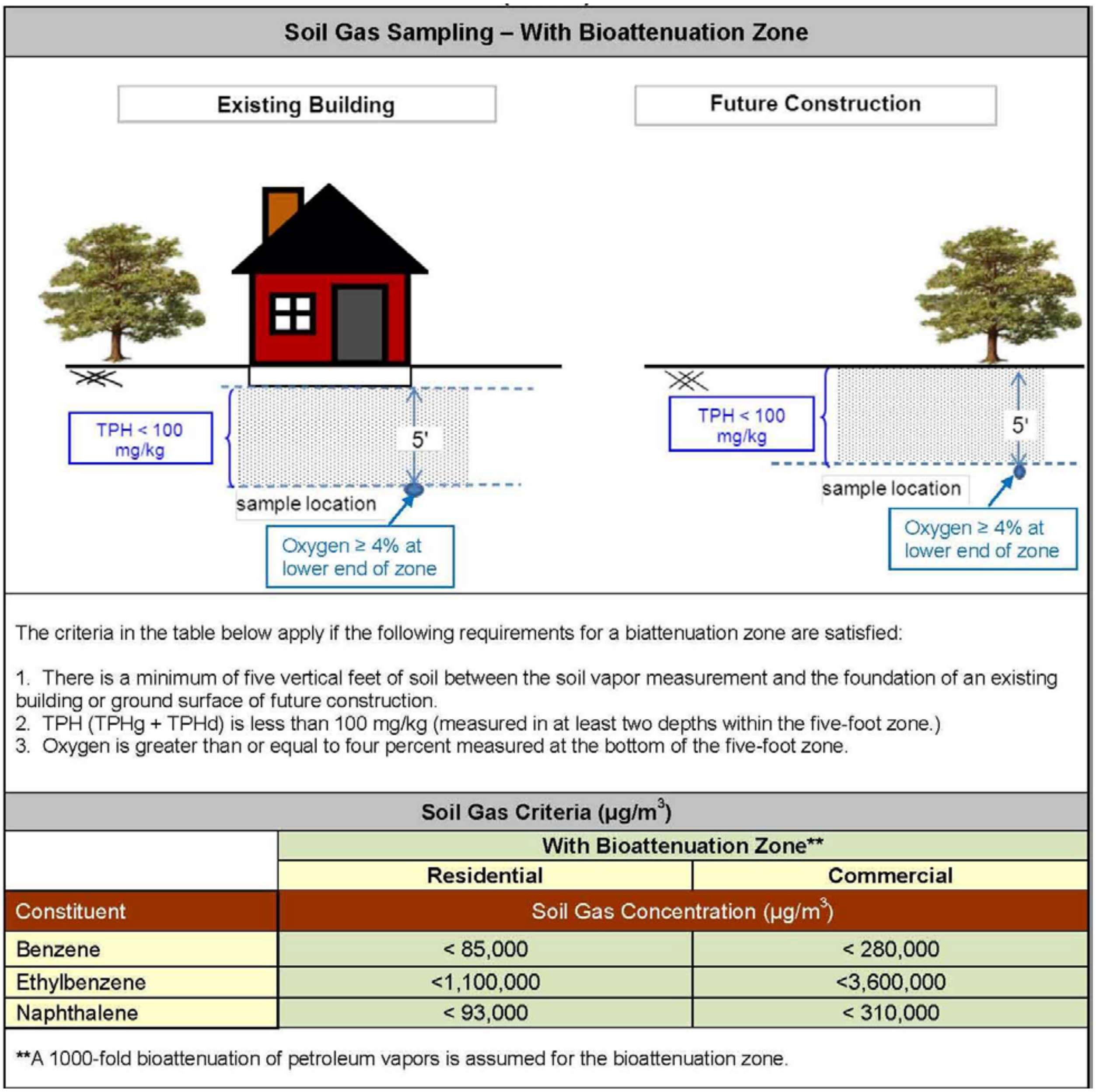
a. Beneath or adjacent to an existing building: The soil gas sample shall be collected at least five feet below the bottom of the building foundation.
b. Future construction: The soil gas sample shall be collected from at least five feet below ground surface.

Soil Gas Criteria (µg/m^3)

	No Bioattenuation Zone*	
	Residential	**Commercial**
Constituent	Soil Gas Concentration (µg/m^3)	
Benzene	< 85	< 280
Ethylbenzene	<1,100	<3,600
Naphthalene	< 93	< 310

*For the no bioattenuation zone, the screening criteria are same as the California Human Health Screening Levels (CHHSLs) with engineered fill below sub-slab.

Figure C-8: Scenario 4b – Direct Measurement of Soil-Gas Concentrations



Soil Gas Sampling – With Bioattenuation Zone

The criteria in the table below apply if the following requirements for a biattenuation zone are satisfied:

1. There is a minimum of five vertical feet of soil between the soil vapor measurement and the foundation of an existing building or ground surface of future construction.
2. TPH (TPHg + TPHd) is less than 100 mg/kg (measured in at least two depths within the five-foot zone.)
3. Oxygen is greater than or equal to four percent measured at the bottom of the five-foot zone.

Soil Gas Criteria (µg/m^3)

	With Bioattenuation Zone**	
	Residential	**Commercial**
Constituent	Soil Gas Concentration (µg/m^3)	
Benzene	< 85,000	< 280,000
Ethylbenzene	<1,100,000	<3,600,000
Naphthalene	< 93,000	< 310,000

**A 1000-fold bioattenuation of petroleum vapors is assumed for the bioattenuation zone.

Table C-3: Vapor Intrusion Pathway Screening at Petroleum Hydrocarbon Sites

Source Characteristics within 30 Feet of Building	Likelihood of Risk Associated with Vapor Intrusion	Recommended Evaluation	Basis for Recommendation	Potential Confounding Factors
Unweathered LNAPL within 30 feet of building structure or dissolved petroleum hydrocarbons in direct contact with building structure	High	Evaluation of safety / explosion hazards. Building evaluation and mitigation, as needed.	This site condition is reported by investigators and regulators as the most common site condition associated with petroleum vapor intrusion sites.	• Impact to structure below depth of building foundation (e.g., dry well, elevator shaft) • Intermittent vapor intrusion associated with high water-table events
Dissolved source (benzene > 1,000 µg/L, with less than 5 feet vertical separation between source and building	Medium	Site-specific evaluation of bioattenuation in vadose zone (e.g., API 2005) and building evaluation, if needed.	• Modeling studies indicate that effectiveness of bioattenuation will be site-specific (API 2009) • Many examples in published literature with high bio-attenuation and no vapor intrusion for this site condition (e.g., Ostendorf and Kampbell 1991) • A review of available field data found >100x attenuation of benzene vapors in the vadose zone for >95% of measurement events (Davis 2006) • VI reported at a few sites with shallow NAPL sources (e.g., Sanders and Hers 2006)	• Poor site characterization fails to identify shallower LNAPL sources • Vapor intrusion associated only with some specific petroleum hydrocarbons (e.g., Sanders and Hers 2006) • Intermittent vapor intrusion • Preferential pathways
Unweathered LNAPL source with greater than 30 ft separation between source and building.	Minimal	No need to assess the VI pathway. See Scenarios 1 & 2	• No published examples of petroleum vapor intrusion for this site condition. • Modeling studies indicate bioattenuation will limit the potential for vapor intrusion (API 2009; DeVaull 2007)	• Poor site characterization fails to identify shallower LNAPL source • Preferential pathways
Dissolved petroleum hydrocarbons (i.e., benzene <1,000 µg/L in groundwater) and greater than 5 feet separation between source and building.	Minimal	Possibly no need to assess the VI pathway. See Scenario 3	• No published examples of petroleum vapor intrusion for this site condition, in contrast to similar chlorinated VOC sites. • Modeling studies indicate bioattenuation will limit the potential for vapor intrusion (API 2009; DeVaull 2007) • Even low O_2 flux into subsurface can meet low O_2 demand from source	• Poor site characterization fails to identify un-weathered residual LNAPL source • Rise in water table brings contamination in contact with foundation • Preferential pathways

Information Regarding Soil Vapor Sampling

Soil vapor sampling is discussed in the Site Assessment chapter of this Manual.

Additional Site Assessment Data

Supplemental data may be helpful for the VI pathway evaluation (API 2005; ITRC 2007; DTSC 2011a). Supplemental data to consider collecting during site investigation include:

1) Soil physical properties data.
2) Building data. An assessment of building construction (e.g., is a vapor barrier present, depth of building foundation, are sump pumps present) and HVAC design and operation may be used to refine the CSM and evaluate whether building factors may limit VI.
3) Surface flux measurements. Surface flux-chamber measurements may be used to evaluate the flux of VOCs to the surface and reduce the uncertainty associated with the diffusion of VOCs through soil.
4) Determination of slab-specific attenuation factor using tracers (e.g., naturally occurring radon).
5) Differential pressure measurements.
6) Real-time and continuous analyzers.

Soil Physical Properties Data

Boring logs and soil samples for physical property analysis (e.g., grain size analysis, soil porosity, volumetric moisture content) can be collected during the installation of the soil-vapor probes. These data will help refine the CSM and may be used for refined VI modeling.

Building Data – Determination of Room Ventilation Rate

The indoor air concentration is inversely proportional to the room ventilation rate: a two-fold increase in ventilation rate decreases the indoor air concentration by two-fold. The default ventilation rates used by the DTSC and many other agencies are conservative: room exchange rates of once every 1 to 2 hours for residences and once every hour for commercial buildings. For some structures, typically commercial buildings, the actual ventilation rate can be determined from the HVAC system or building design specifications, keeping in mind that the air-exchange rate should be calculated from the make-up volume, not the total air-handling volume. For other structures, typically residences, this information is not readily available, so the ventilation rate must be either the default value or it must be measured. ASTM Method E 741 (ASTM 2011) describes techniques for measuring ventilation rates using gaseous tracers such as helium or sulfur hexafluoride (SF_6).

Typically, a pulse input of tracer gas is applied and the decay in concentration versus time is measured. The inverse of the air exchange rate is the slope of a plot of the natural logarithm of the normalized concentration ($C_{t=n}/C_{t=0}$) versus time. If a subsurface tracer gas is used, this can serve as the pulse input. Alternatively, a tracer gas can be released at a constant rate and the concentration measured once steady-state conditions are reached (i.e., typically after three or four air exchanges).

The techniques are quick and relatively inexpensive. For colder climates, measurement during the cold and warm seasons may be prudent if the ventilation rate during the more conservative case (cold season) suggests unacceptable indoor air concentrations.

Surface Flux Chambers

Flux chambers can provide another line of evidence when other types of chemical data (soild gas, groundwater, etc.) are not available or not possible to collect, such as at sites with little to no vadose zone. Discussions of this measurement approach can be found in DTSC (2011b) and in ITRC (2007).

Determination of Slab-Specific Attenuation Factor Using Tracers

Measurement of a conservative tracer inside the structure and in the sub-slab soil gas can allow a site-specific attenuation factor to be calculated. The calculated attenuation factor can then be used to estimate the indoor air concentration of other constituents of concern by multiplying the measured sub-slab soil gas concentration by the attenuation factor for the tracer (or "marker compound"). This method assumes that all sub-slab vapor-phase contaminants are entering the building at equal rates, a relatively safe assumption for most situations. Naturally occurring radon is the most commonly used conservative tracer. Other potential tracers include breakdown products such as 1,1-dichloroethene (1,1-DCE) or cis-1,2-dichloroethene (cis-1,2-DCE), which are generally not found in consumer products, building materials, or outdoor air. Complications to this technique include the presence of indoor sources of the tracer (if any) and any temporal variations. However, if sub-slab samples are being collected, concurrent collection of radon or another tracer data may prove useful and is generally not too expensive. Determination of radon concentration using adsorbents is possible for indoor air samples, but not for soil-gas samples, including sub-slab samples. Soil-gas methods exist for the collection of sub-slab radon concentration measurements (EPA 2006), but analysis of the samples may not be readily available from most commercial laboratories.

Differential Pressure Measurements

Models and look-up values used by the EPA and DTSC are based on assumed advective flow into the structure due to a pressure gradient of 4 Pascals (Pa). This assumption can be checked in the field to provide another line of evidence to evaluate VI using a digital micromanometer attached to a sub-slab soil-gas probe. It is often advisable to use one with data-logging capabilities and assess the response to wind speed and barometric pressure changes if these data are collected.

Measurement of the pressure gradient between the structure and outdoors can assist in interpreting measured indoor concentrations of contaminants. A correlation between indoor air concentration and relative pressure may provide information on the contaminant source. For example, if a building is over-pressured relative to the sub-surface, measured indoor concentrations might be more likely attributed to aboveground sources. Conversely, if the building is under-pressured relative to the sub-surface, measured indoor concentrations might be more likely attributed to sub-surface sources. Commercial buildings with large HVAC systems, and perhaps residences with AC units, may fall into the former category. Many structures in cold environments, especially residences, will fall into the latter category when the heaters are running. This will usually be used as a secondary line of evidence in support of indoor air quality data or other lines of evidence.

Real-Time & Continuous Analyzers

As with any type of site investigation, it is difficult to reach any conclusions with any degree of confidence with only a handful of data points. VI data sets consisting of one soil gas and/or indoor air analysis per structure may be very difficult to interpret, but cost and access limitations often preclude multiple analyses. Real-time analyzers can be used to collect multiple, less expensive data that can be used to locate problem structures, vapor migration routes into structures, and VOC sources inside the structures. Continuous analyzers that collect data automatically over a period of time can sort out background scatter and determine temporal variations both indoor and below-ground. Larger data sets allow trends in the results to be recognized and correlated to other variables such as pressure differentials, wind speed, and HVAC systems. Larger data sets allow forensic approaches to be applied.

A variety of real-time analyzers exist including hand-held logging instruments (PID, FID, TCD, IR analyzers, zNose®, and ppbRAE), automated gas chromatographs, portable mass spectrometers, and the EPA's own trace atmospheric gas analyzer (TAGA).

Note: PID (photo-ionization device, FID (flame-ionization device), TCD (thermal conductivity detector), and IR (infrared) analyzers.

Laboratory Analysis

The analytical methods selected for a VI investigation are dependent upon the regulatory requirements and data quality objectives (DQOs) for a given site. Fixed labs, mobile labs, or field monitoring equipment may be suitable for the purpose, provided that the method detection limits and quality assurance/quality control (QA/QC) are appropriate for the intended use of the analytical results. It is highly advisable to discuss the project specifics with the analytical laboratory prior to the program to ensure that the proper analytical methods are being used and the appropriate sampling hardware and protocols are being used to collect samples.

The recommended target analytes and analytical methods for vapor samples are discussed in the Laboratory Analysis and Methods chapter. Other lists of available methods can be found in ITRC 2007 and API 2005. New guidance from ITRC, scheduled to be released in 2013, is anticipated to contain analytical recommendations.

Data Evaluation

The following steps should be considered in the data-evaluation process (API 2005):

- **Data Organization:** The data should be tabulated and plots developed to summarize the variation of the concentration measurements in space and time.
- **Data Analysis:** The data should be reviewed to assess whether they are consistent with the CSM and internally consistent (i.e., do trends for different constituents behave in a similar manner that is also consistent with the CSM). If the data are not consistent with the CSM, then either update/revise the CSM or verify the data quality. If the data are not internally consistent, then the analytical results may not meet the DQOs for the assessment.
- **Exposure Pathway Assessment:** The data should be reviewed to assess whether the VI pathway is complete. If the pathway is not considered complete, the specific segment (e.g., contaminant source, transport mechanism, exposure point, route of exposure, and/or receptor population) should be identified and documentation / justification provided for this conclusion.
- **Identification of Additional Action:** After the preceding steps are complete, potential additional actions should be assessed. These corrective-action needs may include additional site-characterization data collection, source remediation, implementation of institutional controls, or mitigation measures.

Mitigation

This section gives a brief overview of mitigation options; a detailed discussion of mitigation is discussed in the Remediation chapter. A comprehensive treatment can be found in the DTSC Vapor Intrusion Mitigation Advisory (DTSC 2011b) and the ITRC vapor intrusion guidance (ITRC 2007). The new version of the ITRC vapor intrusion guidance expected to be released in 2013 will contain a section on mitigation for petroleum-specific compounds.

Various different approaches to the mitigation of VI have been proposed and are in use. The DTSC has issued internal guidance on considerations for the implementation of VI mitigation measures for site corrective action programs (DTSC 2011b). When site investigations and/or quantitative risk assessments yield results which indicate the presence of potentially significant health risks associated with the VI exposure pathway, mitigation measures and engineering controls may be used to mitigate both short- and long-term exposure.

Sub-Surface Source Removal

Source-removal efforts serve to reduce the potential for future generation of vapors capable of migrating toward the ground surface and indoor air. This mitigation technique targets the sources of VOC vapors beneath the ground, including those present as solids adsorbed to unsaturated soils, those dissolved in groundwater, or those remaining as NAPLs trapped in the subsurface. Common source-removal options include soil excavation and off-site disposal, *in-situ* chemical oxidation (ISCO), enhanced biodegradation techniques, groundwater extraction and treatment, soil-vapor extraction (SVE), and dual-phase (vapor and water) extraction (DPE), as discussed in the Remediation chapter.

Engineering Controls

HVAC Optimization

A common engineering control implemented as a short- to medium-term solution, or in cases where the potential for VI is considered marginal, is optimization of HVAC operation parameters. This involves modification of parameters such as ventilation rates, as outlined by the American Society of Heating, Refrigerating, and Air Conditioning Engineers (ASHRAE): www.ashrae.org/technology/page/548, in an effort to optimize dilution and improve indoor air quality. This approach must account for ambient outdoor air quality, which is the typical source of the "clean" air used to dilute the otherwise impacted indoor air quality.

Vapor Barriers

In addition to and/or in lieu of residual source removal and HVAC optimization, other types of engineering controls typically target the creation of barriers to migration of vapors through cracks and openings in building foundations. For future buildings slated for construction over VOC plumes, vapor barriers reflect a widely used engineering control for restricting VI through building foundations. Typical vapor barriers include use of polyethylene liners, elevated sub-floors such as Cupolex®, and composite liners such as Geo-Seal™ or Liquid Boot®, often placed beneath the foundation of buildings prior to construction. In certain cases, liquid liners may be introduced on top of existing foundations to seal cracks and/or joints / openings. These barriers serve to fill in and/or cover potential conduits in building foundations, thereby eliminating the potential for migration of vapors to indoor air. Additional methods for creating vapor barriers include:

- Sealing cracks and penetrations
- Spray-on rubberized asphalt membranes
- Aerated floor systems (air-tight raised floor)

The key to barriers is the integrity of the seal; the barriers should survive construction foot traffic, dropped tools, rebar, and poured concrete. Integrity tests should be conducted (smoke tests, indoor air tests) to ensure the efficiency of the system.

Sub-Slab Depressurization Systems (SSDs)

Another category of engineering controls relates to SSDs, which serve a purpose similar to that of vapor barriers, but which achieve their objective by eliminating the pressure differential pulling vapors from the subsurface to indoor air. Specifically, properly designed SSDs serve to maintain a lower pressure beneath the building foundation in comparison to the pressure above the foundation and indoor air, thereby eliminating the pressure gradient governing VI. To achieve this goal, SSDs, which may be installed in existing and/or future buildings, are designed as either active or passive systems. The former utilizes an electric fan or blower, while the latter is vented directly to the atmosphere and may use a roof-mounted, non-powered fan. Active SSD systems typically consist of a fan or blower that draws air from the soil beneath a building, discharging it into the atmosphere through a series of collection and discharge pipes. Holes cut through the building foundation allow for placement of extraction pipes in contact with sub-surface materials, resulting in removal of soil vapor from beneath the building foundation. The exhaust from the blower is generally routed away from windows, doors, or other openings in the building using polyvinyl chloride (PVC) pipe or rain-gutter downspout material.

The above engineering control alternatives for mitigation of VI may be implemented independently or in combination with one another, and are typically supplemented by soil-vapor monitoring or indoor air monitoring to demonstrate the effectiveness of system operations and for protection of public health.

A range of factors should be evaluated in the selection of an appropriate mitigation system to address VI concerns (DTSC 2011b):

- System effectiveness
- Long-term operation and maintenance requirements
- Permitting requirements

- Property owner impacts
- Public participation needs
- Enforcement requirements
- Financial assurance requirements

These factors may influence which technology is selected for VI mitigation at a particular site.

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