<span id="page-0-0"></span>

**Designation: E2531 − 06 (Reapproved 2014)**

### **Standard Guide for Development of Conceptual Site Models and Remediation Strategies for Light Nonaqueous-Phase Liquids Released to the Subsurface<sup>1</sup>**

This standard is issued under the fixed designation E2531; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon  $(\varepsilon)$  indicates an editorial change since the last revision or reapproval.

#### **INTRODUCTION**

This guide provides a framework for developing a light nonaqueous phase liquid (LNAPL) conceptual site model (LCSM) and for using that LCSM in a corrective action decision framework. LNAPLs are most commonly petroleum or petroleum products liquids. Historically, subsurface LNAPL distribution has been conceptualized based on the thickness observed in monitoring wells. However, these conceptualizations often result in an insufficient risk analysis and frequently lead to poor remedial strategies. By using this guide, the user will be able to perform a more appropriate assessment and develop an LCSM from which better remedial decisions can be made.

The design of this guide is a "tiered" approach, similar to the risk-based corrective action (RBCA) process (Guides E1739 and E2081), where an increase in tiers results from an increase in the site complexity and site-specific information required for the decision-making process. The RBCA guides apply to LNAPL and to dissolved and vapor phases. This guide supplements the RBCA guides by providing more information about identifying LNAPL, linking the LCSM to the RBCA process, and describing how the presence of LNAPL impacts corrective action at sites.

In addition to developing the LCSM, the components of this guide will support the user in identifying site objectives, determining risk-based drivers and non-risk factors, defining remediation metrics, evaluating remedial strategies, and preparing a site for closure. If the processes in this guide are adequately followed for sites with LNAPL, it is expected that more efficient, consistent, economical, and environmentally protective decisions will be made.

#### **1. Scope**

1.1 This guide applies to sites with LNAPL present as residual, free, or mobile phases, and anywhere that LNAPL is a source for impacts in soil, ground water, and soil vapor. Use of this guide may show LNAPL to be present where it was previously unrecognized. Information about LNAPL phases and methods for evaluating its potential presence are included in [4.3,](#page-10-0) guide terminology is in Section [3,](#page-2-0) and technical glossaries are in [Appendix X7 and Appendix X8.](#page-61-0) Fig. 1 is a flowchart that summarizes the procedures of this guide.

1.2 This guide is intended to supplement the conceptual site model developed in the RBCA process (Guides [E1739](#page-1-0) and [E2081\)](#page-1-0) and in the conceptual site model standard (Guide [E1689\)](#page-2-0) by considering LNAPL conditions in sufficient detail to evaluate risks and remedial action options.

1.3 Federal, state, and local regulatory policies and statutes should be followed and form the basis of determining the remedial objectives, whether risk-based or otherwise. Fig. 1 illustrates the interaction between this guide and other related guidance and references.

1.4 Petroleum and other chemical LNAPLs are the primary focus of this guide. Certain technical aspects apply to dense NAPL (DNAPL), but this guide does not address the additional complexities of DNAPLs.

1.5 The composite chemical and physical properties of an LNAPL are a function of the individual chemicals that make-up an LNAPL. The properties of the LNAPL and the subsurface conditions in which it may be present vary widely from site to site. The complexity and level of detail needed in the LCSM varies depending on the exposure pathways and risks and the scope and extent of the remedial actions that are needed. The LCSM follows a tiered development of sufficient

 $1$ . This guide is under the jurisdiction of ASTM Committee  $E$ 50 on Environmental Assessment, Risk Management and Corrective Action and is the direct responsibility of Subcommittee [E50.04](http://www.astm.org/COMMIT/SUBCOMMIT/E5004.htm) on Corrective Action.

Current edition approved Nov. 1, 2014. Published December 2014. Originally approved in 2006. Last previous edition approved in 2006 as E2531-06<sup>e1</sup>. DOI: 10.1520/E2531-06R14.

<span id="page-1-0"></span>detail for risk assessment and remedial action decisions to be made. Additional data collection or technical analysis is typically needed when fundamental questions about the LNAPL cannot be answered with existing information.

1.6 This guide does not develop new risk assessment protocols. It is intended to be used in conjunction with existing risk-based corrective action guidance (for example, Guides [E1739](#page-3-0) and E2081) and regulatory agency requirements (for example, USEPA 1989, 1991, 1992, 1996, 1997).

1.7 This guide assists the user in developing an LCSM upon which a decision framework is applied to assist the user in selecting remedial action options.

1.8 The goal of this guide is to provide sound technical underpinning to LNAPL corrective action using appropriately scaled, site-specific knowledge of the physical and chemical processes controlling LNAPL and the associated plumes in ground water and soil vapor.

1.9 This guide provides flexibility and assists the user in developing general LNAPL site objectives based on the LCSM. This guide recognizes LNAPL site objectives are determined by regulatory, business, regional, social, and other site-specific factors. Within the context of the Guide [E2081](#page-10-0) RBCA process, these factors are called the technical policy decisions.

1.10 Remediation metrics are defined based on the site objectives and are measurable attributes of a remedial action. Remediation metrics may include environmental benefits, such as flux control, risk reduction, or chemical longevity reduction. Remediation metrics may also include costs, such as installation costs, energy use, business impairments, waste generation, water disposal, and others. Remediation metrics are used in the decision analysis for remedial options and in tracking the performance of implemented remedial action alternatives.

1.11 This guide does not provide procedures for selecting one type of remedial technology over another. Rather, it recommends that technology selection decisions be based on the LCSM, sound professional judgment, and the LNAPL site objectives. These facets are complex and interdisciplinary. Appropriate user knowledge, skills, and judgment are required.

1.12 This guide is not a detailed procedure for engineering analysis and design of remedial action systems. It is intended to be used by qualified professionals to develop a remediation strategy that is based on the scientific and technical information contained in the LCSM. The remediation strategy should be consistent with the site objectives. Supporting engineering analysis and design should be conducted in accordance with relevant professional engineering standards, codes, and requirements.

1.13 ASTM standards are not federal or state regulations; they are voluntary consensus standards.

1.14 The following principles should be followed when using this guide:

1.14.1 Data and information collected should be relevant to and of sufficient quantity and quality to develop a technicallysound LCSM.

1.14.2 Remedial actions taken should be protective of human health and the environment now and in the future.

1.14.3 Remedial actions should have a reasonable probability of meeting the LNAPL site objectives.

1.14.4 Remedial actions implemented should not result in greater site risk than existed before taking actions.

1.14.5 Applicable federal, state, and local regulations should be followed (for example, waste management requirements, ground water designations, worker protection).

1.15 This guide is organized as follows:

1.15.1 Section [2](#page-2-0) lists associated and pertinent ASTM documents.

1.15.2 Section [3](#page-2-0) defines terminology used in this guide.

1.15.3 Section [4](#page-9-0) includes a summary of this guide.

1.15.4 Section [5](#page-11-0) provides the significance and use of this guide.

1.15.5 Section [6](#page-12-0) presents the components of the LCSM.

1.15.6 Section [7](#page-14-0) offers step-by-step procedures.

1.15.7 Nonmandatory appendices are supplied for the following additional information:

1.15.7.1 [Appendix X1](#page-18-0) provides additional LNAPL reading.

1.15.7.2 [Appendix X2](#page-25-0) provides an overview of multiphase modeling.

1.15.7.3 [Appendix X3](#page-30-0) provides example screening level calculations pertaining to the LCSM.

1.15.7.4 [Appendix X4](#page-36-0) provides information about data collection techniques.

1.15.7.5 [Appendix X5](#page-40-0) provides example remediation metrics.

1.15.7.6 [Appendix X6](#page-42-0) provides two simplified examples of the use of the LNAPL guide.

1.15.7.7 [Appendix X7 and Appendix X8](#page-61-0) are glossaries of technical terminology relevant for LNAPL decision-making.

1.15.8 A reference list is included at the end of the document.

1.16 The appendices are provided for additional information and are not included as mandatory sections of this guide.

1.17 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

1.18 *This guide offers an organized collection of information or a series of options and does not recommend a specific course of action. This document cannot replace education or experience and should be used in conjunction with professional judgment. Not all aspects of this guide may be applicable in all circumstances. This ASTM standard is not intended to represent or replace the standard of care by which the adequacy of a given professional service must be judged, nor should this document be applied without consideration of a project's many unique aspects. The word "Standard" in the title of this document means only that the document has been approved through the ASTM consensus process.*

#### <span id="page-2-0"></span>**2. Referenced Documents**

#### 2.1 *ASTM Standards:*<sup>2</sup>

- [D653](#page-14-0) [Terminology Relating to Soil, Rock, and Contained](http://dx.doi.org/10.1520/D0653) [Fluids](http://dx.doi.org/10.1520/D0653)
- [D6235](#page-9-0) [Practice for Expedited Site Characterization of Va](http://dx.doi.org/10.1520/D6235)[dose Zone and Groundwater Contamination at Hazardous](http://dx.doi.org/10.1520/D6235) [Waste Contaminated Sites](http://dx.doi.org/10.1520/D6235)
- [D5717](#page-64-0) [Guide for Design of Ground-Water Monitoring Sys](http://dx.doi.org/10.1520/D5717)[tems in Karst and Fractured-Rock Aquifers](http://dx.doi.org/10.1520/D5717) (Withdrawn  $2005$ <sup>3</sup>
- [E1689](#page-0-0) [Guide for Developing Conceptual Site Models for](http://dx.doi.org/10.1520/E1689) [Contaminated Sites](http://dx.doi.org/10.1520/E1689)
- [E1739](#page-0-0) [Guide for Risk-Based Corrective Action Applied at](http://dx.doi.org/10.1520/E1739) [Petroleum Release Sites](http://dx.doi.org/10.1520/E1739)
- [E1903](#page-10-0) [Practice for Environmental Site Assessments: Phase](http://dx.doi.org/10.1520/E1903) [II Environmental Site Assessment Process](http://dx.doi.org/10.1520/E1903)
- [E1912](#page-9-0) [Guide for Accelerated Site Characterization for Con](http://dx.doi.org/10.1520/E1912)[firmed or Suspected Petroleum Releases](http://dx.doi.org/10.1520/E1912) (Withdrawn  $(2013)^3$
- [E1943](#page-15-0) [Guide for Remediation of Ground Water by Natural](http://dx.doi.org/10.1520/E1943) [Attenuation at Petroleum Release Sites](http://dx.doi.org/10.1520/E1943)
- [E2081](#page-0-0) [Guide for Risk-Based Corrective Action](http://dx.doi.org/10.1520/E2081)
- [E2091](#page-18-0) [Guide for Use of Activity and Use Limitations,](http://dx.doi.org/10.1520/E2091) [Including Institutional and Engineering Controls](http://dx.doi.org/10.1520/E2091)
- [E2205](#page-9-0) [Guide for Risk-Based Corrective Action for Protec](http://dx.doi.org/10.1520/E2205)[tion of Ecological Resources](http://dx.doi.org/10.1520/E2205)
- [E2348](#page-10-0) [Guide for Framework for a Consensus-based Envi](http://dx.doi.org/10.1520/E2348)[ronmental Decision-making Process](http://dx.doi.org/10.1520/E2348)

2.2 *EPA Standard:*<sup>4</sup>

[EPA Method 8021B](#page-55-0) Aromatic and Halogenated Volatiles by Gas Chromatography Using Photoionization and/or Electrolytic Conductivity Detectors

#### **3. Terminology**

3.1 *Definitions—*Definitions of terms specific to this standard are included in this section, with additional technical terminology provided for reference in [Appendix X7 and](#page-61-0) [Appendix X8.](#page-61-0)

3.1.1 *active remediation, n—*actions taken to reduce or control LNAPL source flux or the concentrations of chemicals of concern in dissolved- or vapor-phase plumes. Active remediation could be implemented when the no-further-action and passive remediation courses of action are not appropriate.

3.1.2 *attenuation, n—*the reduction in concentrations of chemicals of concern in the environment with distance and time due to processes such as diffusion, dispersion, sorption, chemical degradation, and biodegradation.

3.1.3 *chemicals of concern, n—*specific chemicals that are identified for evaluation in the corrective action process that may be associated with a given LNAPL release and are a concern because of potential risk or aesthetic issues.

3.1.3.1 *Discussion—*Identification can be based on their historical and current use at a site, detected concentrations in environmental media and their mobility, toxicity, and persistence in the environment. Because chemicals of concern may be identified at many points in the corrective action process, including before any determination that they pose an unacceptable risk to human health or the environment, the term should not automatically be construed to be associated with increased or unacceptable risk.

3.1.4 *conceptual model, n—*integration of site information and interpretations generally including facets pertaining to the physical, chemical, transport, and receptor characteristics present at a specific site.

3.1.4.1 *Discussion—*A conceptual model is used to describe comprehensively the sources and chemicals of concern in environmental media and the associated risks for particular locations, both now and in the future, as appropriate, at a site.

3.1.5 *corrective action, n—*sequence of actions taken to address LNAPL releases, protect receptors, and meet other environmental goals.

3.1.5.1 *Discussion—*Corrective actions may include site assessment and investigation, risk assessment, response actions, interim remedial action, remedial action, operation and maintenance of equipment, monitoring of progress, making no-further-action determinations, and termination of the remedial action.

3.1.6 *dense nonaqueous phase liquids (DNAPL), n—*nonaqueous phase liquid with a specific gravity greater than one (for example, a chlorinated solvent, creosote, polychlorinated biphenyls).

3.1.7 *engineering controls, n—*physical modifications to a site or facility (for example, slurry walls, capping, and pointof-use water treatment) to reduce or eliminate the potential for exposure to LNAPL or chemicals of concern in environmental media.

3.1.8 *entrapped LNAPL, n—*residual LNAPL in the form of discontinuous blobs in the void space of a porous medium in a submerged portion of a smear zone resulting from the upward movement of the water table into an LNAPL body.

3.1.8.1 *Discussion—*At a residual condition, however, a transient fall of the water table can result in local area redistribution of LNAPL that is no longer in a residual condition.

3.1.9 *exposure pathway, n—*course a chemical of concern takes from the source area to a receptor or relevant ecological receptor and habitat.

3.1.9.1 *Discussion—*An exposure pathway describes the mechanism by which an individual or population is exposed to a chemical of concern originating from a site. Each exposure pathway includes a source or release from a source (for example, LNAPL released from a tank or pipeline), a point of exposure, an exposure route, and the potential receptors or relevant ecological receptors and habitats. If the exposure point is not at the source, a transport or exposure medium (for example, air), or both, are also included.

<sup>&</sup>lt;sup>2</sup> For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

<sup>&</sup>lt;sup>3</sup> The last approved version of this historical standard is referenced on www.astm.org.

<sup>4</sup> Available from United States Environmental Protection Association (EPA), Ariel Rios Bldg., 1200 Pennsylvania Ave., NW, Washington, DC 20460, http:// www.epa.gov.

<span id="page-3-0"></span>

(After Guide [E1739](#page-10-0) and USEPA 2005 (Ref **[1](#page-10-0)**))

NOTE 1—The user is directed to [Fig. 6](#page-16-0) for details of the decision process beginning with identifying LNAPL site objectives. **FIG. 1 Summary of the LCSM Guide**

3.1.10 *facility, n—*property containing the source of the LNAPL or chemical of concern where a release has occurred.

3.1.10.1 *Discussion—*A facility may include multiple sources and, therefore, multiple sites.

<span id="page-4-0"></span>3.1.11 *flux, n—*mass crossing a unit area per unit time in any phase (for example, LNAPL, dissolved-phase, vapor-phase).

3.1.11.1 *Discussion—*Mass flux controls the concentrations potentially reaching receptors and accounts for the depletion of LNAPL bodies through time. See [Fig. 5](#page-8-0) and [Appendix X2](#page-25-0) for more information.

3.1.12 *free LNAPL, n—*LNAPL that is hydraulically connected in the pore space and has the potential to be mobile in the environment.

3.1.12.1 *Discussion—*Often exhibited by LNAPL accumulations in wells. Free LNAPL exceeds the residual saturation. Not all free LNAPL is mobile LNAPL.

3.1.13 *institutional controls, n—*legal or administrative restriction on the use of, or access to, a property so as to eliminate or minimize potential exposure to a chemical of concern (for example, restrictive covenants, restrictive zoning).

3.1.14 *interim remedial action, n—*remedial action taken in the near-term before designing a final remedy to reduce migration of chemicals of concern in the vapor phase, dissolved phase, or LNAPL, or to reduce the concentrations of chemicals of concern or the mass of LNAPL at a source area.

3.1.15 *LNAPL, n—*a light nonaqueous phase liquid having a specific gravity less than one and composed of one or more organic compounds that are immiscible or sparingly soluble in water and the term encompasses all potential occurrences of LNAPL (for example, free, residual, mobile, entrapped). (See [Fig. 2.](#page-5-0))

3.1.16 *LNAPL body, n—*three-dimensional form and distribution of LNAPL in the subsurface existing in all phases (for example, free, residual, mobile, entrapped).

3.1.17 *LNAPL body footprint, n—*two-dimensional form and distribution of LNAPL in the subsurface existing in all phases (for example, free, residual, mobile, entrapped).

3.1.18 *LNAPL body state, n—*status and conditions of the LNAPL body now and in the future, including whether it is geographically stable, mobile, or recoverable.

3.1.18.1 *Discussion—*The estimates of vapor phase and dissolved phase flux from the LNAPL body are also included in the description of the LNAPL body state. It is a dynamic description of the LNAPL body used in risk assessment and remedial action evaluations.

3.1.19 *LNAPL conceptual site model (LCSM), n—* describes the physical properties, chemical composition, occurrence, and geologic setting of the LNAPL body from which estimates of flux, risk, and potential remedial action can be generated.

3.1.19.1 *Discussion—*The LCSM should be a dynamic, living conceptual model (see [3.1.4\)](#page-2-0) that changes through time as new knowledge is gained or as a result of natural or engineered processes altering LNAPL body and ground water and vapor plume conditions. The LCSM can be presented as text or figures, or both.

3.1.20 *LNAPL properties, n—*physical and chemical properties of a specific LNAPL.

3.1.20.1 *Discussion—*Since many petroleum products are composed of multiple chemicals, and because of environmental interactions, both physical and chemical properties can be quite variable between LNAPLs and over time for an LNAPL body at a site, as are the associated potential environmental risks and amenability to different remedial actions.

3.1.21 *LNAPL site objectives, n—*specific set of welldefined, desired outcomes that serve as a basis for remedial action.

3.1.21.1 *Discussion—*For instance, performing an appropriate remedial action should protect human health and relevant ecological receptors and habitats. The corrective action goals defined under a RBCA process are a subset of the LNAPL site objectives. Remediation metrics (specific measurements of the results of the remedial action) are developed to be consistent with the site objectives. Section [7.5](#page-15-0) discusses the LNAPL site objectives in more detail.

3.1.22 *LNAPL type-area, n—*type-area is a description, which may include text, or figures or both, of the geologic, chemical, and LNAPL conditions for a sub-area of a site that represents, or may conservatively represent, the remainder of the site.

3.1.22.1 *Discussion—*Multiple type-areas may be defined for large sites or sites with multiple sources. The intent of using a type-area is to constrain key questions in adequate detail for the type-area, and then apply those findings elsewhere at the site, as appropriate.

3.1.23 *mobile LNAPL, n—*free LNAPL that is moving laterally or vertically in the environment under prevailing hydraulic conditions.

3.1.23.1 *Discussion—*The result of the LNAPL movement is a net mass flux from one point to another. Not all free LNAPL is mobile, but all mobile LNAPL is free LNAPL.

3.1.24 *multi-component, n—*refers to petroleum products or other mixtures composed of many different individual chemicals at varying molar fractions, such as in most petroleumbased fuels, solvents, petrochemicals, and other products.

3.1.25 *natural attenuation, n—*reduction in the mass or concentration of chemicals of concern in environmental media as a result of naturally occurring physical, chemical, and biological processes (for example, diffusion, dispersion, adsorption, chemical degradation, and biodegradation).

3.1.26 *non-risk factors, n—*these are a subset of the desired outcomes that determine the site objectives and they are not strictly based on risks to human health or the environment, although they may have an impact on the risk at a site.

3.1.26.1 *Discussion—*They are often determined by regulations or statutes that are applicable to a site. Examples of non-risk factors include elimination of nuisance conditions and reduction of LNAPL in wells. The non-risk factors should be secondary to risk-based drivers at a site. Section [7.7](#page-15-0) provides additional discussion of the non-risk factors.

3.1.27 *petroleum, n—*including crude oil or any fraction thereof that is liquid at standard conditions of temperature and pressure.

3.1.27.1 *Discussion—*The term includes petroleum-based substances comprised of a complex blend of hydrocarbons derived from crude oil through processes of separation, conversion, upgrading, and finishing (for example, motor fuels, jet oils, lubricants, petroleum solvents, and used oils).



<span id="page-5-0"></span>

NOTE 1—During the early stages of an LNAPL release, LNAPL can be mobile (free) in all zones. NOTE 2—The schematic is intended to convey generalized zones, not the dynamics of an active LNAPL release. **FIG. 2 Illustration of LNAPL Zones**

Nore 1—During the early stages of an LNAPL release, LNAPL can be mobile (free) in all zones.<br>Nore 2—The schematic is intended to convey generalized zones, not the dynamics of an active LNAPL release.<br>**FIG. 2 Illustration** 

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# <span id="page-6-0"></span>**E2531 − 06 (2014)** Air (Non-Wetting **LNAPL** (Intermediate Fluid) **Wetting Fluid)** Water (Wetting Fluid) Soil Grains

LNAPL = light nonaqueous-phase liquid (credit: John L. Wilson, 1990)

#### NOTE 1—Wettability aspects are discussed in [Appendix X2.](#page-25-0) **FIG. 3 Illustration of Residual LNAPL (Immobile) as Identified in a Photomicrograph**

3.1.28 *plume stability, n—*lack of significant geographic movement in the dissolved phase or vapor phase.

3.1.28.1 *Discussion—*The significance of the movement would typically be measured at a scale pertinent to LNAPL site objectives. For example, if a receptor is nearby, then stability would be demonstrated at a finer-scale than if a receptor is at a more distant location in order to meet the LNAPL site objectives. Different phases can have different stability conditions. For example, the LNAPL body may be geographically stable, but dissolved-phase flux emanating from that body may not be stable.

3.1.29 *point of compliance, n—*location selected between the source area and the potential point of exposure, or other relevant location, where remediation metrics are demonstrated to be met (for example, concentrations of chemical of concern at or below the determined site-specific target levels).

3.1.29.1 *Discussion—*Depending on site conditions, multiple points of compliance may be selected for one source area and point of exposure.

3.1.30 *point of exposure, n—*point at which an individual or population may come in contact with a chemical of concern originating from a site.

3.1.31 *reasonably anticipated future use, n—* future use of a site or facility that can be predicted with a high degree of certainty given current use, local government planning, and zoning.

3.1.32 *receptors, n—*persons that are or may be affected by a release (see relevant ecological receptors and habitats for non-human receptor definition).

3.1.33 *recover ability, n—*general term for the degree to which LNAPL can be removed from the subsurface, often defined as the fraction of the total in situ LNAPL mass or of the free or residual volumes.

3.1.33.1 *Discussion—*The recoverability is a function of the in situ LNAPL conditions, the hydrogeologic setting, the type of technology to be used, and the manner in which it is applied.

3.1.34 *release area, n—*area in and around the location where LNAPL was first released to the subsurface.

3.1.34.1 *Discussion—*The source zone is the subsequent subsurface distribution of LNAPL that forms the source term for dissolved- and vapor-phase plumes, as applicable.

3.1.35 *relevant ecological receptors and habitats, n—*ecological resources that are valued at the site.



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Hydrogeologic & Plume Factors

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<span id="page-8-0"></span>

**FIG. 5 Fluxes in Groundwater and Vapor Emanate from the LNAPL**

<span id="page-9-0"></span>3.1.35.1 *Discussion—*Identification of relevant ecological receptors and habitats is dependent on site-specific factors and technical policy decisions. Examples may include species or communities afforded special protection by law or regulation; recreationally, commercially, or culturally important resources; regionally or nationally rare communities; communities with high aesthetic quality; and habitats, species, or communities that are important in maintaining the integrity and bio-diversity of the environment. See Guide [E2205](#page-14-0) for additional discussion.

3.1.36 *remedial action/remediation, n—*activities conducted to protect human health, safety, and the environment.

3.1.36.1 *Discussion—*Included in remedial actions are monitoring programs, activity and use limitations, engineering controls and active clean up systems. Associated with each of the remedial actions are the applicable implementing, operating and monitoring tasks. Remedial actions include activities that are conducted to recover LNAPL, reduce fluxes of chemicals of concern from the LNAPL, reduce sources of exposure, sever exposure pathways, or make other changes to meet LNAPL site objectives.

3.1.37 *remediation metric, n—*specific measurement associated with progress or performance of a remedial action.

3.1.37.1 *Discussion—*Remediation metrics can be cost metrics or benefit metrics. For example, if chemical flux reduction to a receptor were an LNAPL site objective, measurements of flux before, during, and after remediation would be a metric of that remedial action. Other remediation metrics might be a measurement to determine the minimum mobility potential for observable LNAPL, a maximum allowable concentration of an LNAPL chemical of concern at a point of compliance, or a percentile of the potentially recoverable LNAPL.

3.1.38 *residual LNAPL, n—*LNAPL that is hydraulically discontinuous and immobile under prevailing conditions.

3.1.38.1 *Discussion—*Residual LNAPL that cannot move through hydraulic mechanisms (unless prevailing conditions change), but is a source for chemicals of concern dissolved in ground water or in the vapor-phase in soil gas. The residual LNAPL saturation is a function of the initial (or maximum) LNAPL saturation and the porous medium. (See [Fig. 3.](#page-6-0))

3.1.39 *risk assessment, n—*analysis of the potential for adverse human health effects or adverse effects to ecological receptors and habitats caused by the LNAPL or chemicals of concern from a site to determine the need for remedial action or the development of LNAPL site objectives (for example, corrective action goals under a RBCA process) in which remedial action is required.

3.1.40 *risk-based drivers, n—*these are remedial requirements that are based solely on the potential risk to human health or ecological receptors and habitats, as compared to remedial requirements based on other factors (for instance, nondegradation of ground water).

3.1.40.1 *Discussion—*Examples of risk-based drivers include reduction of vapor-phase concentrations to protect people in indoor environments and controlling ground water migration to protect drinking water wells. The risk-based drivers should generally be the priority, while recognizing other factors exist as well.

3.1.41 *risk reduction, n—*lowering or elimination of the level of risk posed to human health or relevant ecological receptors and habitats through interim remedial action, remedial action, or institutional or engineering controls.

3.1.42 *site, n—*area defined by the likely physical distribution of LNAPL and chemicals of concern from a source.

3.1.42.1 *Discussion—*A site could be an entire property or facility, a defined area or portion of a facility or property, or multiple facilities or properties. One facility may contain multiple sites. Multiple sites at one facility may be addressed individually or as a group.

3.1.43 *site assessment, n—*characterization of a site through an evaluation of its physical and environmental context (for example, subsurface geology, soil properties and structures, hydrology, and surface characteristics) to determine if a release has occurred, including the levels of the chemicals of concern in environmental media, the likely physical distribution of LNAPL and chemicals of concern, and LNAPL characteristics.

3.1.43.1 *Discussion—*As an example, the site assessment collects data on soil, ground water and surface water quality, land and resource use, potential receptors, and potential relevant ecological receptors and habitats. It also generates information to develop the LCSM and to support corrective action decision-making. The user is referred to Guide [E1912](#page-2-0) and Practice [D6235,](#page-2-0) and other references in [Appendix X1](#page-18-0) for more information.

3.1.44 *site-specific, adj—*activities, information, and data unique to a particular site.

3.1.45 *smear zone, n—*zone in and around the historic water table where there is residual and potentially free LNAPL that may be above or below the current water table.

3.1.45.1 *Discussion—*The smear zone results from fluctuations of the water table and redistribution of free LNAPL in that zone at sometime in the past or present.

3.1.46 *source zone, n—*three-dimensional zone in the subsurface associated with the release area where LNAPL acts as source for dissolved-phase and vapor-phase plumes of chemicals of concern.

3.1.47 *stakeholders, n—*individuals, organizations, or other entities that directly affect or are directly affected by a corrective action.

3.1.47.1 *Discussion—*Stakeholders include, but are not limited to, owners, buyers, developers, lenders, insurers, government agencies, and community members and groups.

3.1.48 *user, n—*individual or group using this LNAPL guide including owners, operators, regulators, underground storage tank (UST) fund managers, federal or state government case managers, attorneys, consultants, legislators, and other stakeholders.

#### **4. Summary of Guide**

4.1 This LNAPL guide assists in developing an LCSM for making site management decisions. [Fig. 1](#page-4-0) and the following sections summarize the procedure. The figure and text may indicate a linear process; however, as additional data are collected, remedial action is conducted, and knowledge is

#### **TABLE 1 Example LNAPL Indicators**

<span id="page-10-0"></span>Note 1—Items 1 through 3 are direct indicators of LNAPL presence.

NOTE 2—Items 4 through 9 are indirect indicators of potential LNAPL presence.

NOTE 3—The user is encouraged to include additional indicators, as needed.

NOTE 4—Positive responses on indirect indicators increase the likelihood of the presence of LNAPL; additional testing should be conducted to confirm LNAPL presence.

NOTE 5—For any measurement device the reliability of the equipment should be understood (for example, rate of false negatives, rate of false positives) in order to interpret the results.



gained about the LNAPL and the site, the LCSM should be updated and the evaluation processes revisited to incorporate this new information.

4.2 Ensure that immediate or eminent threats and hazards are mitigated. These are conditions such as explosive vapors, flammable materials, or other threatening conditions. State and local regulations and other guidance materials address these facets, as warranted.

4.3 Define the presence or absence of LNAPL based on existing data, if applicable. Table 1 presents some example indicators that individually, or in combination, may suggest the presence of LNAPL at a given site. These are examples only; the list is not comprehensive. The user may develop additional LNAPL screening indicators as technically appropriate. This guide is pertinent to all occurrences of LNAPL, including conditions where it is observable in monitoring wells and where it is not visible, but rather held by capillary forces in the pore space.

4.3.1 LNAPL, where present, is typically the source zone for dissolved- and vapor-phase plumes (that is, assuming that the chemicals of concern that are dissolved in ground water or are volatilized to soil vapor are components of the LNAPL). The LNAPL is often conceptualized as an infinite mass with respect to the dissolved and vapor phases; additional background is included in [Appendix X2](#page-25-0) and [Appendix X4.](#page-36-0) While the infinite mass concept is useful, it is clear that the LNAPL is in fact a finite mass that will change in character through time as a result of natural processes and remedial actions.

4.3.2 Dissolved- and vapor-phase concentrations of chemicals of concern, which are components of the LNAPL, will remain elevated and be complexly and non-linearly related to the concentration or saturation of LNAPL until the amount of LNAPL remaining is less than the mass capacity in other phases (for example, sorbed, dissolved, vapor). When LNAPL ceases to be present, this guide no longer applies.

4.3.3 A schematic of different LNAPL occurrences considered by this guide is shown in [Fig. 2.](#page-5-0) A photomicrograph showing observed residual, immobile LNAPL in soil is shown in [Fig. 3.](#page-6-0)

4.4 Develop a Tier 1 LCSM based on available information and procedures outlined in this guide. [Table 2](#page-11-0) is an example evaluation that provides information to identify the potential level of complexity that may be needed for the LCSM. If key elements of the LCSM cannot be developed because of an absence of information, and those elements are necessary to estimate risks to human health or ecological receptors and habitats, then either additional data collection or a remedial action is warranted.

4.5 Determine whether immediate response actions or initial remedial actions are needed based on Guides E1739 and E2081, and federal, state, and local regulations and policies.

4.6 Determine the appropriate activities for stakeholder involvement and public participation for the site, see Guide [E2348](#page-2-0) and USEPA 2005 **[\(1\)](#page-16-0)** <sup>5</sup> for additional information.

4.7 Determine if the Tier 1 LCSM is adequate to answer risk questions and remedial action questions. Collect additional information and upgrade to a Tier 2 LCSM, if appropriate, or alternatively, elect to perform a remedial action. For the Tier 2 LCSM, define the LNAPL type-area based on LNAPL occurrence, characteristics of the chemicals of concern, and physical properties of the soil and rock. Guide [E1903](#page-2-0) contains additional information about environmental site assessments.

4.8 Determine whether risks to human health or ecological receptors or habitats are present using the site-specific LCSM and the RBCA process detailed in Guides [E1739](#page-14-0) and E2081. Identify the risk-based drivers for the LNAPL site objectives (for example, risk-based screening levels (RBSL), site-specific target levels (SSTL), other relevant measurable criteria (ORMC)). See Guide [E2081](#page-14-0) for further information about risk-based drivers.

4.9 Determine if there are non-risk factors, in addition to the risk-based drivers, for the LNAPL site objectives and remedial action.

<sup>5</sup> The boldface numbers in parentheses refer to a list of references at the end of this standard.

#### **TABLE 2 Example LNAPL Conceptual Site Model Adequacy Checklist**

<span id="page-11-0"></span>NOTE 1—The use of the scoring is site- and regulation-specific. As the complexity of the site increases, the benefit of a detailed LSCM increases. This table is designed to help the user identify what level of complexity, or what tier, for the LSCM is likely to be beneficial to the site. See also [Fig. 4.](#page-7-0)

NOTE 2—The factors should be used to develop a weight-of-evidence to suggest the level of complexity for the LSCM. Sites that have a majority of low scores on the factors would likely fall into a Tier 1 LSCM; sites with mostly low and medium scores on the factors would fall into a Tier 2 LSCM; sites with mostly medium and high scores would fall into a Tier 3 LSCM.





4.10 Enumerate the LNAPL site objectives for the riskbased drivers and non-risk factors in adequate detail such that a remediation strategy may be developed based on the LCSM. Define the remediation metrics and determine which remedial action alternatives may be suitable to achieve the LNAPL site objectives. The LNAPL site objectives and remediation metrics should be consistent with the overall site context and other management or remedial goals that may exist for conditions other than the LNAPL and associated plumes.

4.11 Develop a higher tier LCSM or revise LNAPL site objectives if none of the remedial action options appears to address the LNAPL site objectives, or if there is unacceptable uncertainty in the LNAPL remedial action evaluation.

4.12 Develop a remediation strategy using a remedial action option, or set of options. The remediation strategy should be holistic in that it addresses the risks and considers chemicals of concern in the soluble phase, the vapor phase, and the LNAPL. The remediation strategy is based on the evaluation of the benefits and costs of the considered LNAPL remedial action options and the overall site context of site objectives and remediation metrics.

4.13 Use appropriate technical resources to properly design and install the remedial action elements within the remediation strategy. These remedial engineering aspects are not covered in this guide.

4.14 Monitor the remedial action systems; verify the remediation metrics are met.

4.15 Complete the remedial action or implement long-term monitoring and site management, depending on site context and the remedial action evaluations described in this guide.

#### **5. Significance and Use**

5.1 This guide will help users answer simple and fundamental questions about the LNAPL occurrence and behavior in the subsurface. It will help users to identify specific risk-based drivers and non-risk factors for action at a site and prioritize resources consistent with these drivers and factors.

5.2 The site management decision process described in this guide includes several features that are only examples of standardized approaches to addressing the objectives of the particular activity. For example, [Table 1](#page-10-0) provides example indicators of the presence of LNAPL. [Table 1](#page-10-0) should be customized by the user with a modified list of LNAPL indicators as technically appropriate for the site or group of sites being addressed.

5.3 This guide advocates use of simple analyses and available data for the LCSM in Tier 1 to make use of existing data and to interpret existing data potentially in new ways. The Tier 1 LCSM is designed to identify where additional data may be

<span id="page-12-0"></span>needed and where decisions can be made using existing data and bounding estimates.

5.4 This guide expands the LCSM in Tier 2 and Tier 3 to a detailed, dynamic description that considers three-dimensional plume geometry, chemistry, and fluxes associated with the LNAPL that are both chemical- and location-specific.

5.5 This guide fosters effective use of existing site data, while recognizing that information may be only indirectly related to the LNAPL body conditions. This guide also provides a framework for collecting additional data and defining the value of improving the LCSM for remedial decisions.

5.6 By defining the key components of the LCSM, this guide helps identify the framework for understanding LNAPL occurrence and behavior at a site. This guide recommends that specific LNAPL site objectives be identified by the user and stakeholders and remediation metrics be based on the LNAPL site objectives. The LNAPL site objectives should be based on a variety of issues, including:

5.6.1 Potential human health risks and risks to relevant ecological receptors and habitats;

5.6.2 Specific regulatory requirements; and

5.6.3 Aesthetic or other management objectives.

5.7 This guide provides a framework by which users specify benefit remediation metrics that are consistent and achievable given the conditions of the LCSM.

5.8 Guidance is focused on the information needed to make sound decisions rather than specific methods or evaluations that might be used in deriving that information. This guide is weighted toward field data rather than modeling, though modeling is clearly recognized as a useful tool in generating scenarios and bracketing conditions of the LNAPL body conditions. Limited examples of site specific data used to develop the LCSM are provided in [Appendix X6.](#page-42-0)

5.9 By defining specific, measurable attributes of remedial actions acting upon an LCSM, users can determine which actions may be feasible and which likely are not, using an evaluation of a consistent set of factors and expectations.

5.10 A sound LCSM will lead to better decisions about remedial actions. The site management decision process premised on the LCSM is intended to result in more efficient and consistent decision-making about LNAPL risk evaluations and remedial actions.

5.11 The complexity of multiphase LNAPL issues and the wide variety of analysis and interpretation methods that are available has lead to uncertainty in decision-making regarding sites with LNAPL and has sometimes resulted in misleading expectations about remedial outcomes.

5.12 Current risk assessment methods often assume the LNAPL is an infinite source of chemicals of concern. The remediation decision-making may be better defined by considering the LNAPL as the source material for chemicals of concern by explicitly characterizing the chemical composition and physical characteristics of the LNAPL body.

5.13 When LNAPL presents the main source of risk, the LNAPL should be the primary target of remedial actions and those remedial actions should be determined by following the decision evaluations described in this guide.

5.14 LNAPL regulatory policies that define remediation metrics by small LNAPL thicknesses in wells are, on a site-specific basis, often inconsistent with risk-based screening levels (RBSLs) and with current technical knowledge regarding LNAPL mobility and recoverability. LNAPL remediation metrics should be connected to the current or potential future exposures and risks, as well as to other non-risk drivers present for a particular site.

5.15 The user of this guide is encouraged to identify the appropriate process for public involvement and stakeholder participation in the development of the LCSM and the site management decision process.

5.16 By providing a flexible framework, this guidance will continue to be applicable in principle while the many unknowns and uncertainties in LNAPL movement and the associated risks in all plume phases (for example, sorbed, dissolved, vapor) are studied through future research efforts. Like the LCSM itself, this is a "living" document that must embrace advances in knowledge and in technology.

#### **6. Components of the LNAPL Conceptual Site Model**

6.1 The LCSM describes the physical properties, chemical composition, and setting of the LNAPL body from which assessments of flux, risk, and potential remedial action can be generated. The LCSM is a dynamic, living model that will change through time as new knowledge is gained or as a result of natural or engineered processes altering conditions. The goal of the LCSM is to describe the nature, geometry, and setting of the LNAPL body and associated dissolved-phase and vaporphase plumes in sufficient detail so that questions regarding current and potential future risks, longevity, and amenability to remedial action can be adequately addressed.

6.2 The LCSM is developed in a tiered fashion. The level of complexity and refinement of the LCSM, including the complexity of the various specific aspects of the LCSM, are determined based on the questions to be answered at each tier of the assessment (as in the RBCA tiers). The Tier 1 LCSM is developed based on existing site knowledge and using generic assumptions about LNAPL behavior. The Tier 2 LCSM includes some simple site-specific analyses. The Tier 3 LCSM may include more complex evaluations and modeling for any aspect of the LCSM.

6.3 In general the LCSM includes:

6.3.1 LNAPL physical characteristics and chemical composition;

6.3.2 Information about the horizontal and vertical location of the LNAPL body;

6.3.3 Hydrogeologic conditions, history, and properties, and the distribution of those properties;

6.3.4 Information to determine if the LNAPL is mobile at the scale of the LNAPL body footprint (for example, comparisons of the LNAPL body geometry over time);

6.3.5 Information about exposure pathways and potential receptors and relevant ecological receptors and habitats under current and future use scenarios; and

<span id="page-13-0"></span>6.3.6 Specific components of the LCSM are discussed further in 6.6.

6.4 The complexity and level of detail in the LCSM follows a tiered approach. [Table 2](#page-11-0) provides an example LCSM checklist that can be used to assess the needed complexity of the LCSM. The user can customize [Table 2](#page-11-0) to include more factors or information that may be relevant to a specific site or class of sites. The example table can be used to develop a weight-ofevidence determination for the level of complexity needed in the LCSM. Factors that can affect the relative complexity of the LCSM are shown in [Fig. 4.](#page-7-0)

6.4.1 *Tier 1 LCSM—*These are sites where new or existing standard site assessment data are sufficient to describe risk conditions and potential remedial action alternatives. The complexity and level of detail required in the LCSM is likely to be low. These sites may have the lowest scores (for example, a majority of low scores) on the [Table 2](#page-11-0) example LCSM checklist. To develop a Tier 1 LCSM:

6.4.1.1 Use existing information, as available for sites that have had historic site assessment activities, including but not limited to soil and ground water sampling, fluid level gauging, boring logs, hydrogeologic testing, release and operations history, and other related information.

6.4.1.2 For sites with no existing information, collect sufficient data to construct a Tier 1 LCSM. Use [Table 2](#page-11-0) to assist in considering whether a more advanced LCSM is needed for the specific site conditions to ensure data collection efforts, as needed, are executed at the appropriate level of detail and density. This is applicable at any stage of this process where additional data are determined to be necessary.

6.4.2 *Tier 2 LCSM—*These are sites where the Tier 1 LCSM is inadequate to address the risk and remedial action questions that need to be answered. In these cases, the level of detail required in the LCSM is greater. Sites in this category may also require more advanced evaluations of costs and benefits for remedial action alternatives for the selection of applicable remedial action alternatives. These sites may have mid-level scores (for example, a majority of low and medium scores) on the [Table 2](#page-11-0) example LCSM checklist.

6.4.3 *Tier 3 LCSM—*By definition, if a Tier 2 LCSM has been developed and site assessment, risk assessment, or remedial action questions cannot be answered with existing information, or where it is important to reduce uncertainties, then additional data collection is needed and a more detailed Tier 3 LCSM is developed. These sites may have the highest scores (for example, mostly medium and high scores) on the [Table 2](#page-11-0) example LCSM checklist.

6.4.4 At any juncture, a remedial action can be implemented in lieu of additional data collection or analysis resulting in higher LCSM tiers. This option would be based on the user's judgment in context with the remedial decision process. If a remedial action is more direct, cost-effective, or otherwise warranted, the user could opt for that action and would not need to develop higher LCSM tiers. However, insufficient understanding of the site can lead to inaccurate remedial decision-making, so it is still recommended that the LCSM be developed at a level of detail that is adequate for the remedial objectives and decisions.

6.5 The LCSM forms the basis for LNAPL corrective action decisions.

6.6 Specific components of the LCSM are presented in this section. The descriptions for each component span the range from Tier 1 through Tier 3 LCSM. [Fig. 5](#page-8-0) is a schematic of the components that should be addressed in the LCSM. One or more of the components may be unknown or have limited information. If a potential lack of information directly affects a risk assessment or remedial action decision, then additional data or information should be collected. Conversely, if that lack of information has no impact on the risk assessment or remedial action decision, then there would be little or no value to additional data collection.

6.6.1 *Release Source and Timing—*What happened or may have happened during the LNAPL release (for example, location, rate, timing) provides information that may be useful in developing an understanding of the LNAPL body. Its age, conditions of the release and timing assist interpretations about the LNAPL geometry, stability, chemical composition, flux, and other related issues.

6.6.2 *Geometry of the LNAPL Body—*To make flux and risk estimates and to evaluate the potential success of a remedial action for an LNAPL body, the geometry of the LNAPL body must be known in sufficient detail to address these questions.

6.6.2.1 To understand the geometry of the LNAPL body, define the top, bottom, and lateral dimensions of the LNAPL body through direct or indirect observations.

*(1)* Direct observations could include detectable LNAPL, sheens, emulsification, or oil droplets, or visual signs of LNAPL.

*(2)* Indirect observations could include ground water or soil vapor concentrations at or near effective solubility or volatility limits, fluorescence in the appropriate ranges, volatility readings, dye testing, or passive sampling of ground water for chemicals of concern at different elevations in wells. The reliability of the indirect measurements (for example, rate of false positives and false negatives) should be considered when interpreting the results from these methods. Often confirmation of indirect results is needed through direct measurement methods. Advances in technology may expand the potential list of available measurement tools and their application in the future.

6.6.3 *LNAPL Chemical Composition and Physical Characteristics—*The chemical composition of the LNAPL and site physical characteristics define the risk and play a key role in estimating mobility and amenability to specific types of remedial action. These characteristics include:

6.6.3.1 Chemicals of concern for risk evaluations;

*(1)* To understand the LNAPL chemical composition and physical characteristics, define the chemical makeup of the LNAPL body through direct or indirect analytical measurements taken within the LNAPL body.

*(a)* Direct measurements include laboratory analyses of soils or LNAPL; LNAPL may be extracted from soil cores and need not come only from liquid-phase sampling.

*(b)* Indirect measurements may include inferences drawn from the chemical composition of the dissolved or vapor phase plumes in contact with the LNAPL source, or from other

<span id="page-14-0"></span>indirect methods such as geophysical characterization or knowledge about the original released materials.

6.6.3.2 General chemistry for total lifespan and remedial action questions; and

6.6.3.3 Physical properties of the LNAPL (for example, viscosity, interfacial tension density) for mobility, recoverability, and remedial action evaluations.

6.6.4 *Ground Water and Hydrogeologic Conditions—*The ground water and hydrogeologic setting of the site play a key role in identifying the important exposure pathways, estimating mobility and amenability to specific types of remedial action. The ground water and hydrogeologic conditions to consider include:

6.6.4.1 Properties and distribution of soil and rock materials;

*(1)* To understand the soil and rock conditions, define the physical properties of the soil and rock materials that affect chemical flux, transport, and remedial action (for example, hydraulic conductivity, dispersivity, porosity, density, capillarity, tortuosity, organic content). Additional information is available in Terminology [D653.](#page-2-0)

6.6.4.2 Ground water and hydrologic conditions (for example, gradient, piezometric variability, climatic conditions).

*(1)* To understand the ground water conditions, define the aquifer and vadose zone features pertinent to flux and potential receptors. These may include factors like effective diffusion coefficients, sorption, degradation half-lives, and others that affect the fate and transport of chemicals to those potential receptors.

6.6.5 *Receptors and Location Characteristics—*The receptor characteristics and their locations relative to the LNAPL body are important to defining the exposure pathways. The information needed includes:

6.6.5.1 Human receptors, relevant ecological receptors and habitats, and resource receptors, see Guides [E1739,](#page-16-0) [E2081,](#page-15-0) and [E2205](#page-2-0) and USEPA 1989 **[\(4\)](#page-40-0)** for additional information;

6.6.5.2 Conditions now and likely in the future, including changing land use; and

6.6.5.3 Definition of remedial action timeframe and future uncertainties.

6.6.6 *Estimated Chemical Fluxes or Concentrations in All Phases at Points of Compliance—*An understanding of the concentrations or fluxes in the vapor phase and the dissolved phase at each of the points of compliance is important in determining the actions that are needed for the site.

6.6.7 *Definition of the Mobility or Stability Conditions of the LNAPL Body, Ground Water, and Vapor Plumes—*The condition of the LNAPL body (for example, is the LNAPL body stable, contracting, or expanding?) is important for understanding the risks and the potential remedial action needed for the site.

#### **7. Procedure**

7.1 LNAPL, depending on its physical properties and chemical composition, can present immediate concerns for flammability, vapor intrusion, explosivity, and other imminent dangers. Those concerns are dealt with directly by the responsible parties based on regulatory requirements or guidance documents, and while included for context, they are not the focus of this guide.

7.2 Define the presence or absence of LNAPL, and its occurrence (for example, free LNAPL, residual LNAPL; [Figs.](#page-5-0) [2 and 3\)](#page-5-0). If there is no LNAPL present, this guide does not apply. LNAPL presence may be determined from direct or indirect information such as measurement of free LNAPL in wells, LNAPL body or ground water plume persistence, center-of-mass stability, or other relevant features. [Table 1](#page-10-0) presents some example indicators that individually, or in combination, may suggest the presence of LNAPL at a given site. These are examples; the list is not comprehensive. The user may develop different or additional LNAPL screening indicators as technically appropriate.

7.3 Develop the LCSM. The specific tier of the LCSM is determined based on the information presented in [6.4](#page-13-0) and [6.6](#page-13-0) and the following sections.

7.3.1 Develop a Tier 1 LCSM that includes the information listed in [6.4.1](#page-13-0) using known or reasonably available site data and information. When one of the RBCA standard guides is used at a site, the Tier 1 LCSM would be developed in parallel with the RBCA Tier 1.

7.3.2 Develop a Tier 2 LCSM, addressing the information in [6.4.2](#page-13-0) where critical elements are unavailable and cannot be adequately interpreted from the existing or easily obtainable data (for a Tier 1 LCSM). In particular, if the Tier 1 LCSM is inadequate to evaluate risk and remedial action options, a Tier 2 LCSM should be developed. When one of the RBCA standard guides is used at a site, the Tier 2 LCSM would be developed in parallel with the RBCA Tier 2.

7.3.3 Develop a Tier 3 LCSM, addressing the information in [6.4.3](#page-13-0) where critical elements are unavailable and cannot be adequately interpreted from the simple site-specific analyses conducted for the Tier 2 LCSM. In particular, if the Tier 2 LCSM is inadequate to evaluate risk and remedial action options, a Tier 3 LCSM should be developed. When one of the RBCA standard guides is used at a site, the Tier 3 LCSM would be developed in parallel with the RBCA Tier 3.

7.3.4 When additional data are collected at a site, including data collected during remedial action implementation and operation, the LCSM should be updated to account for the additional data and observations, regardless of the specific tier where the LCSM development was completed.

7.3.5 For sites where a Tier 2 or Tier 3 LCSM is developed, determine the type-area distribution of LNAPL mass and chemicals of concern based on the LCSM.

7.3.5.1 The type-area concept is used in recognition of the complexity of LNAPL distribution in the subsurface, limitations in data availability in some areas (for example, operations or offsite), and the often poor accuracy with which LNAPL mass can be estimated.

7.3.5.2 The type-area should be reflective of known conditions, such as the concentration history of chemicals of concern in ground water and other attributes. The type-area should acknowledge and describe uncertainties in known conditions so as to support appropriately conservative and protective corrective action at the site.

<span id="page-15-0"></span>7.3.5.3 The type-area is documented using cross-section figures or text descriptions, or both.

7.3.5.4 Bracketing a range of potential conditions around the type-area is useful in presenting the LCSM and constraining uncertainty.

7.4 Implement immediate response actions or initial remedial actions, as needed, based on the data collection and analysis completed in developing the LCSM.

7.5 Define the LNAPL site objectives including risk-based drivers and non-risk factors that impact remedial requirements. [Fig. 6](#page-16-0) shows the details of the decision-making process, which includes defining the LNAPL site objectives, identifying remediation metrics, and selecting a subset of remedial options that have a probability of meeting those objectives.

7.5.1 The LNAPL site objectives are the specific reasons that remedial action is needed. For instance, one reason for performing an appropriate remedial action may be that it protects human health and the environment. Protection of human health is the highest priority for remedial action, but other LNAPL site objectives are often important, too, and should be considered. This prioritization may affect the timing of one or more remedial actions.

7.5.2 The LNAPL site objectives are defined as a subset, and in the context, of the overall site objectives for corrective action.

7.5.3 The LNAPL site objectives are defined so that the basis of completion of any remedial action can be defined before the action is undertaken. The LNAPL site objectives combined with the LCSM provide a basis for feasibility evaluations of potential remedial actions.

7.5.4 From the LNAPL site objectives, more detailed remediation metrics are defined that are specific measures of the outcome of the remedial action. These can be viewed as performance measurements.

7.5.5 Site objectives should be specific and not open-ended.

7.5.6 The user should define a process by which the values and preferences of the stakeholders are taken into account in determining the site objectives.

7.5.7 The desired time frame and locations at which each site objective will apply should be stated.

7.5.8 Where there are subjective or broad remedial requirements (for example, user preferences, stakeholder concerns), they should be broken down into specific LNAPL site objectives.

7.6 Identify the potential risk-based drivers for setting LNAPL site objectives.

7.6.1 Use one of the RBCA guides (Guides [E1739](#page-25-0) and [E2081\)](#page-40-0) to estimate the risk-based screening levels (RBSL), site-specific target levels (SSTL), or site-specific ecological criteria (SSEC) appropriate for the site.

7.6.2 Use an alternative and accepted risk-based method to estimate the potential risks to human health, ecological receptors and habitats, and environmental resources (as applicable to the receptor setting) in accordance with local, state, and federal regulations and guidance.

7.7 Determine if there are non-risk factors for defining LNAPL site objectives from applicable local, state, or federal regulations or guidance, or company policies. If so, the specifics of such additional requirements should be determined. The potential non-risk factors should be clearly identified, along with the basis for completion of a remedial action. Examples of non-risk factors may include:

7.7.1 Reduction of LNAPL mass;

7.7.2 Reduction of observable LNAPL in wells;

7.7.3 Mitigation of nuisance conditions;

7.7.4 Reduction of LNAPL body mobility;

7.7.5 Reduction of longevity of chemicals of concern sourced from the LNAPL;

7.7.6 Reduction of flux from dissolved phase or vapor phase plumes;

7.7.7 LNAPL mass recovery to a specific engineering limit;

7.7.8 Business drivers; and

7.7.9 Other community concerns.

7.8 Once the LNAPL site objectives have been identified, the LCSM can be reviewed to determine if any of the LNAPL site objectives are met under the current site conditions.

7.9 If the data and information collected from [7.2](#page-14-0) and [7.3](#page-14-0) are insufficient to determine the LNAPL site objectives, upgrade to a higher tier LCSM or implement an interim remedial measure, if appropriate, to address key issues, including:

7.9.1 Plume stability or mobility evaluations of the LNAPL body and associated dissolved phase or vapor phase plumes (see Guide [E1943](#page-2-0) for further information regarding dissolvedphase plume stability);

7.9.2 Flux conditions for chemicals of concern;

7.9.3 Amenability and expectations for remedial actions;

7.9.4 Natural mass losses from the LNAPL body; and

7.9.5 Plume longevity for chemicals of concern and nuisance considerations.

7.10 For a Tier 2 or Tier 3 LCSM, additional data collection would generally include multiphase characterization data. Multiphase data collection can be challenging because of complexity and nonlinearity in multiphase mechanics, and the expense of collecting site-specific data (for related information, see [Appendix X2 – Appendix X4\)](#page-25-0).

7.10.1 More than typical site assessments, multiphase characterization to support the LCSM requires detailed planning and an evaluation of the value of the data being collected.

7.10.2 Often, data collection is an iterative process where working LCSM hypotheses are described, data are collected to support or refute working hypotheses, the working model is updated, and potential additional data needs are considered. The following are some specific questions to ask before embarking on multiphase data collection efforts:

7.10.2.1 What specific LCSM, risk, or remedial action questions cannot be addressed with existing information?

7.10.2.2 Have existing data, including historical or current remediation response data (as applicable), been fully evaluated from a multiphase/multi-component perspective? Has a thorough attempt been made at building and testing an LCSM with the existing information?

7.10.2.3 What is the value of the answers to be derived relative to the cost of additional data collection?

<span id="page-16-0"></span>

**FIG. 6 Detailed Procedures**

<span id="page-17-0"></span>7.10.2.4 What is the degree of geologic and LNAPL body heterogeneity, and will the proposed data collection be of sufficient density and quality to reflect that underlying variability?

7.10.2.5 Are parameters to be collected in support of modeling, and if so, have the methods of data collection and analysis been compared to the assumptions of the model?

7.10.2.6 Have the limitations of discrete sampling and laboratory methods been considered with respect to their potential affect on LCSM understanding?

7.10.3 [Appendix X4](#page-36-0) includes more information about data collection in two broad categories: delineation and parameter determination, and potential uses of the information to enhance the LCSM.

7.11 Select remedial action alternatives for consideration. The potential remedial actions are developed based on the LCSM and the specifics of the LNAPL site objectives through evaluations not covered by this guide.

7.11.1 Remedial action evaluations may include engineering and hydrogeologic analysis of remediation mechanics as pertinent to the LCSM and LNAPL site objectives.

7.11.2 Potential remedial action alternatives are those that have attributes capable of meeting the combined LNAPL site objectives.

7.11.3 USEPA; API; federal, state, and local agencies; and other industry resources are available to assist in selection of potential remedial action alternatives (see additional LNAPL references in [Appendix X1\)](#page-18-0).

7.12 Define the remediation metrics. There are two categories of remediation metrics: those based on the benefits to be gained from the remedial action and those based on the costs associated with the remedial action. The remediation metrics are used to quantitatively evaluate the remedial action alternatives.

7.12.1 The benefit remediation metrics may include factors such as:

7.12.1.1 Facets of chemical longevity associated with the LNAPL;

7.12.1.2 Changing chemical distribution through time;

7.12.1.3 Flux-based levels in the vapor or dissolved phase;

7.12.1.4 Concentration-based targets; and

7.12.1.5 LNAPL thickness targets.

7.12.2 The cost remediation metrics may include factors such as:

7.12.2.1 System equipment power use;

7.12.2.2 Raw materials and capital equipment use;

7.12.2.3 Land-use impairment to the community or business;

7.12.2.4 Affect on ground water use and storage;

7.12.2.5 Wastes generated or relocated by the remedial action system;

7.12.2.6 Potential environmental impacts; and

7.12.2.7 Remedial action monetary costs.

7.12.3 Often the benefit remediation metrics will apply to many different remedial action alternatives (for example, an indoor air site-specific target level), whereas the cost remediation metrics will often be specific to the different remedial

action alternatives (for example, excavation and institutional controls would have different cost remediation metrics).

7.12.4 The point of compliance for each benefit remediation metric should be clearly identified (that is, where, how, and when measurements will be made to compare to the remediation metric). In addition, the data analysis, field tests, and laboratory methods used for the remediation metrics should be specified.

7.12.5 The selected remediation metrics should correspond directly to the LNAPL site objectives.

7.12.6 The remediation metrics should be specific and quantifiable.

7.12.7 The remediation metrics should express the aspects of LNAPL remedial action that are essential for the specific site and are important to the user and stakeholders.

7.12.8 In conjunction with the remedial alternatives analysis, well-defined remediation metrics will indicate the probability of each remedial action reaching the specific benefit remediation metrics, in what time frames, and with what costs and benefits.

7.13 For each remedial action alternative, the specific benefits and costs of the action should be listed. [Appendix X5](#page-40-0) includes examples of the benefits and costs to be listed and the level of detail to be used.

7.13.1 Each remedial action alternative should be evaluated in enough detail to determine whether the benefit remediation metrics can be met using the alternative.

7.13.2 The probability of success of the remedial action alternative and the costs associated with a failure of the remedial action meeting the benefit remediation metrics should also be assessed.

7.13.3 If, at any point in the evaluation, key outcomes of the considered remedial action cannot be defined due to uncertainty in either the LCSM or in the mechanics of the remedial action, additional data gathering or new technical evaluations should be implemented.

7.13.4 For a remedial action to be carried forward in the remedial decision evaluation, the benefits should outweigh the costs for each potentially viable action.

7.14 The outcome of the comparison of the benefits and costs may be that there are no feasible remedial action alternatives that will achieve the LNAPL site objectives (see [Fig. 6\)](#page-16-0).

7.14.1 In these cases, the LNAPL site objectives should be re-evaluated by the user and the stakeholders to determine if changes are necessary.

7.14.2 It may also be necessary to upgrade to a higher tier LCSM and implement the data collection and analysis steps in [6.6,](#page-13-0) [7.9,](#page-15-0) and [7.10](#page-15-0) using more complex and detailed methods.

7.14.3 The user would return to 7.11 and redefine potential remedial action alternatives and continue through the procedure. If no feasible alternatives can be identified, the user would go to [7.20](#page-18-0) where a long-term management plan should be considered.

7.15 Using ASTM, USEPA, RTDF, API, and other remedial action guidance documents, compare remedial action alternatives using the benefit and cost remediation metrics (See additional LNAPL references in [Appendix X1\)](#page-18-0).

<span id="page-18-0"></span>7.15.1 This process may be implemented using a simple scoring system or may require a sophisticated decision analysis to account for uncertainties in the input variables and the outcomes of the remedial action methods. The complexity of the decision analysis process is determined by the user. [Appendix X5](#page-40-0) includes an example of a simple decision scoring system for comparing alternatives.

7.15.2 The remedial options comparison should include such factors as the time of operation, overall costs, land-use needs, probability of success, and other factors. There will be sites where shorter duration remedial actions are warranted and others where long-term remedial action is more applicable.

7.15.3 With adequate certainty in the analysis, the most viable option will be the one that has the highest benefits with the lowest costs, dependent on site conditions including landuse, regulatory context, funding, and required remedial action time frames.

7.16 Choose the remedial action alternative that best balances the benefit and cost factors and is acceptable to the stakeholders.

7.17 Implement selected remedial action.

7.17.1 During implementation, the remedial action should be monitored and operational conditions compared to the remediation metrics to demonstrate progress toward meeting the LNAPL site objectives. This tracking will also help identify needed enhancements to the remedial action, update the understanding of the LCSM, and demonstrate progress toward completing the remedial action.

7.17.2 The LCSM should be re-evaluated during the remedial action implementation to reflect the increased knowledge of the LNAPL body and the subsurface environment as a function of remedial outcomes observed. The data collection and analysis steps in [6.6,](#page-13-0) [7.9,](#page-15-0) and [7.10](#page-15-0) should be revisited and the LCSM updated as appropriate.

7.18 When the remediation metrics have been met and the LNAPL site objectives have been achieved and demonstrated, the site has completed the process in this guide. There may be other corrective action or completion requirements for the site that are outside the scope of this guide.

7.19 If the remediation metrics are not met as planned, or the LNAPL site objectives have not been achieved, the user has two options to consider:

7.19.1 Re-evaluate original LNAPL site objectives and corresponding remediation metrics and go through the procedure again to consider whether additional remedial actions are warranted.

7.19.2 Re-evaluate the LCSM with the additional understanding generated from the remedial action and update accordingly. A key implication of not achieving LNAPL site objectives is that the LCSM or the remedial action mechanics were not representative when the initial evaluations were completed. Remedial action, in this sense, provides additional characterization feedback on the LCSM.

7.20 If remedial action is not feasible, or when feasible actions are complete, the site may move into a long-term monitoring and management program, depending on other potential corrective action requirements for the site. Guide [E2091](#page-2-0) includes information regarding the use of activity and use limitations at sites.

7.21 [Appendix X5](#page-40-0) includes additional discussion of LNAPL remediation metrics and a decision analysis example used to compare remedial action alternatives based on all of the available information.

#### **8. Keywords**

8.1 conceptual site models; corrective action decision framework; light nonaqueous phase liquids; petroleum releases; remedial action decision-making; risk-based corrective action

#### **APPENDIXES**

#### **(Nonmandatory Information)**

#### **X1. ADDITIONAL LNAPL READING**

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<span id="page-25-0"></span>*Chemicals in Groundwater: Prevention, Detection and Restoration*, Houston, TX, November 1993.

#### **X2. OVERVIEW OF MULTIPHASE MODELING**

X2.1 *Introduction*—Multiphase modeling is a tool that can be used to assist in LCSM building and decision-making. The technical roots of multiphase modeling are in petroleum reservoir and agricultural simulations in which movement of multiple fluid phases is critical to the problems being solved. Modeling is a mathematical representation of the underlying physics or chemical conditions or both in the multiphase, multicomponent system. Understanding modeling concepts enhances the user's understanding of the interrelationships in the environmental system and the sensitivity of various parameters. It also provides an appreciation for the complexity and uncertainty in that system.

X2.1.1 The purpose of this appendix is to provide the user with a basic summary of multiphase modeling and an introduction to common simplifying assumptions. This may assist the user in determining the methods and tier level in which the multiphase modeling may be appropriate for a given site. Use of multiphase and other models requires sufficient skill and background of the user. If users are unfamiliar with these methods, they should seek a qualified professional to implement the multiphase modeling or define an alternate field-based program to determine necessary answers to risk assessment and remedial action questions.

X2.1.2 This appendix is intended to compliment Appendix X3 in Guide [E1739](#page-30-0) (RBCA, 1995, 2002 reauthorization). All general modeling principles discussed in that guide apply here and are not reiterated, except where necessary.

X2.1.3 Additional sources of information about multiphase modeling are included in the LNAPL references in [Appendix](#page-18-0) [X1.](#page-18-0)

X2.1.4 Environmental subsurface modeling is complex. There are additional complexities in multiphase modeling beyond those that are discussed in this appendix. Overall, these complexities, combined with a general lack of site-specific multiphase parametric control data, suggest the potential for significant uncertainty in modeling results. For this reason, this guide recommends an orientation toward reliance on field data, supported by multiphase modeling where needed, and appropriate evaluation of modeling results.

X2.1.5 More so than other fields of modeling, multiphase modeling results are highly nonlinear and seemingly consistent results can be generated from incorrect parameter assumptions associated with an inaccurate LCSM. Therefore, there should be a stronger dependence on field data and multiple lines of evidence for evaluating the consistency of physical and chemical multiphase modeling results. The benefit of multiphase modeling is that it can assist in testing the various aspects of the LCSM and can help elucidate key physical and chemical processes that will affect decisions at a particular site.

X2.1.6 The LCSM is the fundamental foundation of any multiphase modeling, regardless of modeling complexity (Tier 1, 2, or 3).

X2.2 *Scope*—This appendix discusses primary categories of multiphase modeling, recognizing that there are crossover models that may have elements of each category to solve the problems envisioned by the code authors.

X2.2.1 For each category of multiphase modeling, this appendix outlines some of the general constraining assumptions in that particular method. Many of these modeling methods are applicable to both light and dense NAPL conditions. However, the discussion here is limited to application for LNAPL.

X2.2.2 This appendix does not outline multiphase modeling procedures, as those are too varied and complex for inclusion.

X2.2.3 [Appendix X3](#page-30-0) includes some examples of simple multiphase approximation techniques and equations that may be used to understand better LNAPL distribution, volume, potential mobility, and recoverability. [Appendix X4](#page-36-0) includes information on field data collection.

X2.2.4 A list of typical parameters and knowledge usually needed for multiphase modeling is given in [Table X2.1.](#page-26-0)

X2.3 *Precautionary Statements* —For any model, multiphase or otherwise, the key assumptions, limitations, and boundary conditions must be understood and the user should recognize the constraints of the selected model as it is applied to the specific site. Violation of the fundamental constraints calls into question the validity of the calculation results.

X2.3.1 Since in-situ multiphase properties and distributions are often difficult to measure and understand, it is often unknown whether specific model constraints are met in the subsurface without extensive investigation, calibration, and validation efforts.

X2.3.2 Simple analytical approximations may assist in understanding, but should not be expected to have a high degree of accuracy. Further, without sound user judgment, results may be misleading.

X2.3.3 Because of inherent complexity, constraining assumptions, data limitations, and novelty in application to environmental conditions, multiphase modeling is as much an art as a science. Significant interpretation and judgment are required to develop an accurate and compelling picture.

X2.3.4 Because of the complexity of multiphase modeling, the person implementing the modeling should be a qualified professional.

X2.3.5 The following sections focus on the LNAPL phase, while recognizing the principles also apply to other subsurface fluid phases (for example, soil vapor and groundwater).

X2.4 *Multiphase Model Selection Criteria*—There are several factors to consider when selecting the best model(s) to solve multiphase problems. Some relevant questions are:

#### **TABLE X2.1 Common Multiphase Modeling Parameters (Partial list, compositional model requirements not included)**

<span id="page-26-0"></span>Note 1—The determination of sensitivity is general and subjective and will not hold in all cases. The basis for these suggested sensitivity levels is derived primarily from modeling results using the associated parameters. In some cases, parameters have an indirect relationship to flux/risk/cleanup. The user should develop site-specific sensitivity ranges that are appropriate at higher tiers.

Note 2—API Publication 4711 [\(5\)](#page-39-0); Methods for determining inputs to environmental petroleum hydrocarbon mobility and recovery models. A useful resource in identifying specific parameter testing methods.

NOTE 3—When a particular parameter becomes important to determining site risk or other factors, one would either conservatively bracket that parameter from literature values or refine the estimates through site-specific measurements (higher tier).





**TABLE X2.1** *Continued*

<span id="page-27-0"></span>

X2.4.1 What specific questions need to be answered and are model-constraining assumptions consistent with those?

X2.4.2 What is the data/parameter availability to constrain modeling?

X2.4.3 Are the initial conditions known, such as the timing, rate, and magnitude of an LNAPL release or other relevant driving event?

X2.4.4 For what phases and for what components will flux estimates be needed?

X2.4.5 How resolved and accurate do the answers need to be?

X2.4.6 What cost and level of effort is needed to address adequately the specific questions to be answered?

X2.4.7 Is the model benchmarked, peer-reviewed, and demonstrated to be accurate within the assumptions of the specific method?

X2.4.8 Who is the audience (for example, regulatory agency, stakeholders) for modeling results, and are they in agreement with the approach, methods, and analysis tools selected?

X2.4.9 Can key questions and objectives be answered through data collection rather than modeling?

X2.4.10 Can key questions and objectives be answered through simple analytical models and data collection, to provide multiple lines of evidence, rather than using more complex numerical models?

X2.4.11 What are the potential risks and consequences if the modeling is wrong?

X2.4.12 Are all important processes germane to the problem considered by the selected model?

X2.4.13 Are transient conditions important?

X2.4.14 Does the modeler have requisite understanding of the tools being applied and the underlying physics and numerical solution methods?

X2.4.15 Is the model input/output procedure repeatable by others and adequately documented?

X2.5 *Physical Basis for Multiphase Modeling*—Multiphase models account for the hydraulic interactions of multiple fluids in the pore space, typically water, vapor, and LNAPL (implicitly or explicitly, depending on the model).

X2.5.1 The most flexible and general form of multiphase modeling is compositional analysis in which conservation of mass, energy, and momentum form the rigorous basis for calculations in three dimensions. The complexity and nonlinearity of the compositional models present practical challenges in application. However, all other forms of multiphase modeling, as discussed below, result from simplifications to these more general conditions, which may not be representative in all cases. As with all modeling, reducing the scope of the calculations is warranted only when the processes eliminated are inconsequential to the questions being asked.

X2.5.2 The most commonly applied numerical multiphase models for environmental simulations solve the continuity equation for mass conservation, which describes the mass movement of any phase in any direction for a nondeforming coordinate system (after Huyakorn et al, 1994 **[\(6\)](#page-67-0)**). Nondeforming system constraints imply that key underlying fluid and soil properties are intrinsic to the formation and do not vary as a function of time or transformation through other reactions:

$$
\frac{\partial}{\partial \chi_i} \left[ k_{ij} k_{ip} \frac{\rho_p}{\mu_p} \frac{\partial \Phi}{\partial \chi_i} \right] = \frac{\partial}{\partial_i} \left( \Theta \rho_p S_p \right) - M_p \tag{X2.1}
$$

*∂* = differential operator,

where:



X2.5.3 Despite the complexity of Eq X2.1, the principles it represents are easily described. Phase movement in any primary Cartesian direction, represented by the left side of Eq X2.1, is controlled by the fluid and soil properties (that is, effective phase conductivity) and the gradient at any point in

space. Net movement into or out of an elemental volume must be equaled by a coincident change in mass within that volume (that is, the right side of Eq  $X2.1$ ). If either the phase conductivity or gradient are zero, there is no phase mobility. The fluid potential Φ includes a gravity term, and it is sometimes assumed that the matrix is rigid or nondeforming; this is not always true in fine-grained or compressible materials. The other factors can be ascribed parametric values. This is the fundamental equation approximated by multidimensional transient multiphase simulators, with more tightly constrained numerical and analytical solutions possible by assuming more restrictive boundary conditions (for example, steady-state, radial symmetry, vertical equilibrium, and others).

X2.6 *Specific Discharge and Seepage Velocity*[—Eq X2.1](#page-27-0) indicates that LNAPL plume conditions are transient. Under limiting conditions, one may sometimes assume that steadystate conditions are present and that Darcy's Law can be used (specific discharge). To do so, there must be either no mass transfer (static plume), or the rate of flux is everywhere uniform throughout the body (constant rate of change). For the second condition to be true, a continuing release would be needed so that the flux crossing any boundary is equaled by the flux input into the system. Clearly, use of Darcy's Law for multiphase conditions is a limited approximation.

$$
V_n = -\frac{k_r k_{ij} \frac{\rho g}{\mu} i_n}{\Theta_{en_n}} = -\frac{K_n \cdot i_n}{\Theta_{en_n}}
$$
 (X2.2)

$$
q_n = -k_r k_{ij} \frac{\rho g}{\mu} i_n = -K_n \cdot i_n \tag{X2.3}
$$

X2.6.1 If one assumes that a steady-state approximation might hold, then Darcy's law could be applied to derive the Darcy flux (specific discharge =  $q_n$ , see Eq X2.3) and the average LNAPL velocity (seepage velocity =  $V_n$ , see Eq X2.2). Note that the negative sign represents a vector direction, flow being from high head to low. The specific discharge is the mathematical product of conductivity and gradient, which for LNAPL includes all the complications previously discussed. Its physical meaning is the volume per unit area moving across a theoretical boundary. The actual movement or velocity, however, occurs only through the interconnected pore space containing NAPL (seepage velocity, Eq X2.3). The factors in Eq X2.2 and X2.3 have been previously defined, except for  $i_n$ , which is the head potential gradient in the NAPL phase, Θ*en*. In turn , 1*en* is the effective porosity toward the NAPL phase (Θ*en*  $S_n \cdot \Theta$ , and the subscript *n* in the flux equations refers to the NAPL phase.

X2.6.2 The Darcy and seepage velocity equations (Eq X2.2) and X2.3) contain several well-understood parameters including fluid density, viscosity, soil intrinsic permeability, and gravitational acceleration. The key factors that are less commonly used are relative permeability, LNAPL saturation, and the LNAPL gradient, as discussed in the following. These factors are typically considered in one form or another by multiphase models that perform the estimates of phase movement. The reader is directed to the additional reading in [Appendix X1](#page-18-0) for more detailed descriptions.

X2.7 *LNAPL Saturation*—Saturation defines the fractional presence of any fluid in the pore space at any given time. For instance, an LNAPL saturation of 0.25 means that 25 % of the pore space contains LNAPL. If the soil porosity were 40 %, then 25 % of that 40 % is filled with LNAPL for a total LNAPL content of 10 % by volume in this example. Integration (summing) of the LNAPL volumetric content vertically and laterally yields an estimate of total volume of the LNAPL plume. The saturation and volumetric content can be estimated through direct measurement, through interpretation, through modeling, or by assuming vertical equilibrium (VEQ) conditions associated with an observed LNAPL thickness in a well and estimating the volume through soil/fluid capillary relationships.

X2.8 *Wetting and Nonwetting Phases*—Capillary relationships describe the wetting and nonwetting phase saturations as a function of the capillary pressure between phase couplets (water-LNAPL, LNAPL-vapor, water-vapor). For instance, as the pressure of LNAPL increases relative to the pressure in the water phase (typically the wetting fluid), the water saturation decreases and the LNAPL saturation increases. So, a large and rapid LNAPL release with a high driving pressure would typically result in higher soil LNAPL saturations than a small release over longer duration, all other things being equal.

X2.8.1 Relative permeability is scalar from 0 to 1 that increases exponentially with phase saturation. For example, at residual LNAPL saturation, the relative permeability toward LNAPL is zero. From Eq X2.2 and X2.3, the movement (flux) is also zero, irrespective of the other parameter values such as high intrinsic soil permeability.

X2.8.2 Combined, the mathematical product of the intrinsic soil permeability, relative permeability, density, gravitational acceleration and the inverse of viscosity yield the effective hydraulic conductivity to LNAPL or other phases at those particular conditions. From the preceding discussion, it should be clear that effective phase conductivity is not a constant of the geologic formation as is the case in pure groundwater flow, but rather it varies as a function of the saturation and associated relative permeability toward the fluids of interest.

X2.8.3 Combined with the capillary implications of variable LNAPL saturation laterally and vertically, it is clear that these aspects alone present significant uncertainty in predictive multiphase modeling.

X2.8.4 The LNAPL hydraulic gradient is directly analogous to the groundwater gradient. The NAPL gradient, or fluid potential head over distance, is a combination of the LNAPL elevation and pressure head. This is the driving force behind LNAPL movement. If the gradient were zero, then irrespective of the LNAPL effective conductivity, there would be no plume movement.

X2.8.5 For a variety of reasons, including capillary effects and water-wet soil resistance to LNAPL movement, the LNAPL gradient is often different than the groundwater gradient, frequently with a mounded radial signature.

X2.8.6 For the purposes of field determination of the LNAPL lateral gradient, mapping of the LNAPL phreatic <span id="page-29-0"></span>surface derived from surveyed well-gauging data is the most direct estimate method, analogous to determination of the groundwater gradient. It should not be assumed *a priori* that LNAPL flow is in the same direction or magnitude as groundwater flow. That assumption is predominantly false, although there are locations in which the LNAPL and groundwater gradients are similar in form and magnitude.

X2.8.7 A second LNAPL gradient approximation can be derived if one assumes LNAPL in a well is in vertical hydrostatic equilibrium with the formation and the water table. Under this condition, one need only know the LNAPL density to determine the elevation above the corrected water table. For instance, at a density of 0.75 g/cc, a 1-ft (0.3-m) LNAPL well thickness will be present 0.25 ft (0.08 m) above the corrected groundwater table (that is, the groundwater elevation in the absence of LNAPL).

X2.9 *Types of Multiphase Models* —From a formulation perspective, there are three categories of multiphase models: analytic, semi-analytic, and numerical, with associated increasing sophistication and problem solving capability. In general, simpler models are often best used to bracket ranges of conditions and consider parameter sensitivity to the results.

X2.9.1 Analytic models are discrete mathematical functions with exact solutions that are typically constrained by several simplifying assumptions. Their advantage is that they can elucidate specific processes and the exact solution provides for short computation times, so many iterations can be executed to assist the interpretive process. Analytic approximations are typically derived by sequential simplification of the differential equations associated with the continuity equation or other equations of state in compositional models. Analytic models typically require the least parameter input and often consider homogeneous conditions, but they require the greatest discretion and interpretation of results as applied to actual field conditions.

X2.9.2 Hybrid semi-analytic models typically combine some simplifying attributes of analytic approximations with one or more flexibilities associated with numerical methods for more complex components of the problem being solved. These models have higher input requirements and offer more refined estimates of LNAPL mobility, recovery, chemical flux, or other attributes of interest.

X2.9.3 Numerical models are the least constrained by temporal, boundary, or spatial restrictions and are essentially a differential approximation to the underlying physical and chemical equations. Parametric properties can vary in time and space, and transient conditions are readily accommodated. Data input requirements are high, and knowledge of the physics and chemistry of the problems being solved is typically required. These models can, in principle, produce the most representative results of hydraulic or chemical conditions. However, their complexity can lead to a greater potential for incorrect use and adds to the effort required for both input and output even when they are being used in their simplest mode with assumptions comparable to analytical solutions. This is particularly so in multiphase modeling in which multiple

parametric models are required to solve the problem. For example, gradient, saturation, conductivity, and movement of LNAPL are all related, and a change in one causes changes in the rest.

X2.10 *Types of Problems that Can Be Solved*—With any of the methods discussed in this appendix, the problem solving involves multiphase hydraulics and multicomponent partitioning and transport from the LNAPL. The problem solving needed, as well as the model selected, depends on the questions being asked and the availability of input parameters. For instance, if an LNAPL body were known to be immobile through field information, perhaps one would select a partitioning and transport model to tie the LNAPL chemistry to flux and potential risk in groundwater or vapor. If the key questions revolve around LNAPL stability or recoverability, one might select a hydraulic multiphase model that need not have a chemical transport component.

X2.10.1 For any of the generalized modeling methods in [X2.2,](#page-25-0) there are a variety of computational solution techniques that influence model run times, model stability, mass balance, and other factors. The user is directed to the references in [Appendix X1](#page-18-0) for additional information about LNAPL.

X2.11 *Commonly Assumed Modeling Conditions*—Because of the complexity of multiphase modeling in general, a wide variety of simplifying assumptions are made to reduce the formulation effort and the input data requirements. The potential variants are many, and this list includes just a few commonly used in environmental multiphase simulation. As mentioned, this appendix does not discuss computational solution methods.

X2.11.1 For virtually all analytical multiphase models, the Dupuit assumptions are invoked. The earth system is homogeneous and isotropic. The LNAPL "aquifer" is radially infinite. The simplicity of these and other constraining assumptions renders these models inaccurate in complex or heterogeneous settings (that is, most settings). However, much can often be learned through bracketing parameter ranges and simulation conditions.

X2.11.2 Many models are steady-state, using piecewise estimates of instantaneous movement when transient approximations are desired. In the latter case, multiphase flow conditions are considered steady over an allotted time increment, with flow/mass conditions updated at each time step. When accurate transient evaluations are important, these models may not be appropriate. These models are typically used for quick screening approximations of LNAPL mobility or recoverability.

X2.11.3 *Vertical Hydrostatic Equilibrium—*This is an assumed condition whereby at all times there is no vertical gradient (that is, instantaneous vertical equilibration of the LNAPL phase). Lateral movement is assumed to occur under those equilibrium conditions. When components of delayed vertical drainage or nonequilibrium effects are important, these methods are inappropriate.

X2.11.4 *Areal 2-D Models—*The key assumption of areal (2-D) models is vertical equilibrium. Some vertical equilibrium <span id="page-30-0"></span>models allow heterogeneity through vertical integration of the saturation, relative permeability, intrinsic permeability, and capillary profiles at any place in the area of interest. This allows for a map-view model that has an implicit third dimension. The limitations of the method are similar to those in  $X2.11.1 - X2.11.3$ 

X2.11.5 *Sharp Interface Method—*In this approach, the LNAPL is assumed to form a uniform layer above the water table, with some approaches accounting for buoyancy and others not. Many, but not all, of the models of this class recognize partial saturation and relative permeability toward the LNAPL or water phases. Invoking this assumption basically allows a solution of simple layered flow expressions. This method does not agree well with field/laboratory multiphase conditions and is a gross screening methodology.

X2.11.6 *Piece-Wise LNAPL Layering—*In this extended analytic method, the LNAPL is embedded into slab layers in the model, with each layer being internally uniform but potentially variable between layers. The model then estimates migration or recovery of the LNAPL phase on a layer-wise basis and recompiles the layer results at each time step, accounting for changes in mass distribution and regenerating the model layers for each new time step.

X2.11.7 *Dimensional Simplification—*Many models conserve mathematical effort by compressing 3-D space into some smaller geometric representation. Some models are 1-D (plug movement), some are 2-D cross sectional, some are 2-D radially symmetric, and some are psuedo-3-D with implicit vertical movement between layers, constrained by interlayer conductivity to transfer, and horizontal flow in transmissive layers.

X2.11.8 *Phase Reduction—*Many multiphase models do not consider the active movement of all three fluid phases (water, LNAPL, and vapor). Commonly, advective vapor movement is ignored, and sometimes LNAPL is treated as a static chemical source term for partitioning estimates to groundwater and vapor. Clearly, in cases in which phase movement is important, one cannot ignore phases of interest.

X2.11.9 *Mathematical Solution to Numerical Models—* Numerical models solve the problem on complex mathematical grids/meshes, regardless of dimensionality, through finitedifference, finite-element, or finite-volume methods. Specifics of solution algorithms are not discussed here.

X2.11.10 *Rigid Matrix—*A common assumption of many multiphase analytical and numerical models is that the soil matrix is rigid. Recall from the continuity equation that a key assumption is for a nondeformational system (that is, rigid). When material properties and controlling parameters may be affected by soil deformation, phase chemical or physical transformations, thermal variations, or other complex processes, such solution methods are not fully applicable, and compositional modeling approaches are needed. Some models allow for matrix compressibility and storage effects but without alteration of the intrinsic properties like permeability, capillarity, and others.

X2.11.11 *Compositional Models—*These models have the greatest problem-solving flexibility and can allow interrelationships between many properties, including thermodynamic variations. For instance, fluid viscosity and density change with temperature and potentially with LNAPL weathering. A compositional model can accept mathematical relationships for these factors to be included in the solution. Typically, a compositional model performs mass balance checking on individual components of interest as they move among and with the fluid phases that exist in the subsurface.

X2.12 *Multiphase Modeling Summary* —There are a variety of factors to consider before embarking on multiphase modeling efforts. The complexity and limitations of the calculation methods are important in context with the problems to be solved. Consistent with Guide [E1739,](#page-34-0) conservatism and bracketing ranges of conditions are recommended when multiphase modeling is selected as a tool to understand better site LNAPL conditions. A strong reliance on site data and its relationship to the various multiphase and multicomponent transport processes will assist in producing useful and informative results.

#### **X3. EXAMPLE CALCULATIONS**

X3.1 *Introduction*—This appendix provides examples for screening estimates of various multiphase and multicomponent conditions important to the LCSM and site decision-making. As mentioned in [Appendix X2,](#page-25-0) these simple methods are not comprehensive, nor are they necessarily appropriate for specific sites.

X3.1.1 The purpose of these examples is to illustrate some simple methods, to assist the user in "getting started" in the LCSM building process, and to help the user understand better what is needed for a particular site.

X3.1.2 User judgment and skill are required for these and other more complex calculations and estimates. Incorrect assumptions, boundary conditions, or parameter selection will result in erroneous and misleading results. Use of the following methods or others, interpretations, and the effect on decisionmaking are solely and fully the responsibility of the user.

X3.2 *LNAPL Distribution*—As noted in the procedures section of this guide, the distribution and the geometry of the LNAPL body are integral components to the LCSM. The following approaches can assist in evaluating the vertical and lateral distribution of LNAPL.

X3.2.1 *Use of Site Soil Total Petroleum Hydrocarbons (TPH) Analytical Data—*Where site analytical data for soil samples exist for TPH in a specific fuel range (for example, gasoline, diesel, oil), these data may be used to estimate the LNAPL saturation distribution if the data are of sufficient density and quality.

X3.2.1.1 TPH is related to saturation by:

$$
S_o = \frac{\left[TPH\right]}{1 \times 10^6} \cdot \frac{\rho_{fb}}{\rho_o} \cdot \Theta^{-1}
$$
\n(X3.1)

<span id="page-31-0"></span>where:

*TPH* = concentration in mg/kg,

 $\rho_{tb}$  = field bulk density of the soil,

$$
\rho_o
$$
 = oil density of the particular LNAPL, and

 $\Theta$  = soil total porosity.

*(1)* This calculation yields the LNAPL saturation at one point in space.

X3.2.1.2 Cautions in use of this conversion include verifying that the TPH spectrum analyzed encompasses the full range of hydrocarbons present, recognizing that laboratories typically sub-sample soil under field conditions, and that the field bulk density depends on both dry bulk density and liquid content. The user should also be certain the soil TPH measurements are representative of the LNAPL intervals of concern, which is often not the case in the smear zone in which LNAPL distribution is heterogeneous on a small scale and sampling can be difficult using standard soil collection techniques.

X3.2.1.3 To estimate the vertical saturation distribution, the user should inspect the TPH data sets and other related data, like historic water levels and LNAPL observations, to interpret the top and bottom of this interval, as well as the potential distribution of LNAPL saturation.

X3.2.1.4 To determine the lateral distribution, the user should inspect the TPH results in cross section or in three dimensions to interpret the extent. Again, other related information such as groundwater concentrations, boring logs, field headspace screening, historic presence of LNAPL in wells, and other related features can assist in this interpretation.

X3.2.2 *Vertical Equilibrium Model Estimates—*Under conditions of vertical hydrostatic equilibrium, the LNAPL observed in wells can be used to determine the vertical distribution of LNAPL saturation at each well location containing free LNAPL (Farr et al, 1990 **[\(7\)](#page-67-0)**; Lenhard et al, 1990 **[\(8\)](#page-67-0)**). To use this method, the user should know the soil and LNAPL capillary parameters, and the observed LNAPL thicknesses in wells.

X3.2.2.1 From the equilibrium LNAPL thickness in a well, the user can derive the capillary head between the fluid couplets of interest, oil-water couplet below the air/oil interface in a well, oil-air couplet above that interface, and water-air couplet once LNAPL ceases to be present in the capillary fringe. The following sequence of equations is used:

X3.2.2.2 Capillary pressure head is derived for each fluid couplet and zone:  $h_{aw} = Z_{aw}$ ;  $h_{ao} = (\rho_{ro}) Z_{ao}$ ;  $h_{ow} = (1 - \rho_{ro}) Z_{ow}$ where *h* is the capillary head; the subscripts *a*, *w*, and *o* designate the couplets for air, water, and oil (LNAPL), respectively, and *Z* is the elevation above the reference datum (oil-water, air-oil, or air-water interfaces, respectively).

X3.2.2.3 Using the capillary pressure and capillary van Genuchten equations (1980) **[\(9\)](#page-61-0)**, saturations are determined for each fluid pair zone:

$$
S_e = \left[1 + \left(\alpha_{ij}h_{cij}\right)^N\right]^{-M} \tag{X3.2}
$$

where:

 $S_e$  = effective wetting phase saturation defined as:

$$
S_e = \frac{\Theta - \Theta_r}{\Theta_m - \Theta_r}
$$
 (X3.3)

where:



*(1)* The capillary α value, if known for one fluid pair (commonly air-water), can be scaled to other fluid pairs by the ratio of the interfacial tensions. For instance, to convert the air-water capillary  $\alpha$  to the oil-water system,

$$
\alpha^{\sigma w} = \alpha^{\sigma w} \frac{\sigma_{\sigma w}}{\sigma_{\sigma w}}
$$
 (X3.4)

where:

 $\sigma_{ii}$  = interfacial tension for the given fluid couplet (air-water and oil-water in this case).

*(2)* The same would be calculated for the air-oil couplet, namely:

$$
\alpha^{ao} = \alpha^{aw} \frac{\sigma_{aw}}{\sigma_{oa}} \tag{X3.5}
$$

X3.2.2.4 Or alternatively, another capillary equation (Brooks-Corey) (Ref **[\(10\)](#page-61-0)**) might be used:

$$
S_e = \begin{bmatrix} \Psi_{b_{ij}} \\ \Psi_{c_{ij}} \end{bmatrix}
$$
 for  $\Psi_c > \Psi_b$ , else  $S_e = 1.0$  (X3.6)

where:

 $\Psi_b$  = bubbling pressure (also know as entry pressure),

- $\Psi_c$  = capillary pressure for the appropriate fluid couplet (see above), and
- $\lambda$  = pore sorting index, analogous to the *N* value in the prior capillary equation.

*(1)* Eq X3.6 is a step-function in which the wetting phase saturation  $= 1.0$  for all capillary pressures less than the entry pressure. As above, the entry pressure should be scaled for each fluid pair of interest.

X3.2.2.5 The full LNAPL saturation profile is assembled based on the capillary pressures and capillary equations (see [Fig. X3.1,](#page-32-0) LNAPL saturation profiles for two different sandy soils). These profiles can then be integrated vertically to derive the specific volume (volume per unit surf area) of LNAPL  $(V_o = \Theta^{\frac{nuf}{f}} S_o dz$ , where  $V_o = \text{oil}$  specific volume (volume/area) integrated from the base to the top of LNAPL).

NOTE X3.1—Because specific volume dimensionally reduces to units of length  $(L^3/L^2 = L)$ , it is often and erroneously thought of as a "thickness" exaggeration" term. This is incorrect. The LNAPL thickness or vertical distribution in the formation, under equilibrium conditions, is always greater than the thickness measured in a well irrespective of the soil or LNAPL properties. Vertical exaggeration as a result of heterogeneity and

<span id="page-32-0"></span>**LNAPL Saturation**  $\n **Run 1 - LNAPL** Saturation\n$  $\n **Run 2 - LNAPL**\n**Saturation**$  $2.2$  $2.0$  $\widehat{E}$ Elevation Above OIL/Nater Interface<br>
Elevation Above Oil/Nater Interface<br>
0.8<br>
0.8<br>
0.4  $0.2$  $0.0$  $0.2$  $0.0$  $0.1$  $0.3$  $0.4$  $0.5$  $0.6$  $0.7$  $0.8$ **LNAPL Saturation** 

**E2531 − 06 (2014)**

NOTE 1—Finer-grained materials will have smaller saturation values.

**FIG. X3.1 LNAPL Distribution Under Vertical Hydrostatic Equilibrium Conditions at 1-m Well Thickness for Two Sandy Materials**

nonequilibrium conditions can occur but would then violate the key assumptions of the hydrostatic methods above (that is, they would be inapplicable).

X3.2.2.6 Mapping the specific volume values areally will allow the user to estimate the total volume. This volume estimate does not include residual LNAPL that is not in communication with the well (laterally or vertically) unless accounted for separately. While there is no vertical thickness exaggeration under hydrostatic equilibrium conditions (discussed above), there is a volume exaggeration implied by the thickness of LNAPL measured in a well. This is because the well is a macropore that contains 100 % LNAPL above the water levels in the well. In the formation, however, the LNAPL saturations are less than 100 % (see Fig. X3.1), and the integrated volumes are generally much smaller than might otherwise be implied by the well conditions.

X3.2.2.7 *Cautions—*As discussed, this method for estimating total LNAPL volume assumes that the LNAPL in wells is at hydrostatic equilibrium. This is not always the case under dynamic field conditions. To test this, the user should characterize the LNAPL distribution and pressures in the formation through drilling or other techniques. Even where local equilibrium is present, there may be residual LNAPL below and above the vertical equilibrium interval that is not accounted for in the estimate unless it has already been identified in the field measurements or observations. While the aquifer and vadose residual saturation values can and should be considered, the user should have data or reason to know those zones are present, since they are not generally indicated by the LNAPL in wells. The user might use historic fluid level fluctuations to assist in considering the distribution of residual LNAPL, as well as soil analytical data and other indicators.

X3.2.3 *LNAPL Body Stability Considerations—*It is important to recognize that a finite body of LNAPL cannot spread infinitely in porous media. Some of the mass is retained as residual LNAPL in the soil, and this trapping of LNAPL means that a finite volume can maximally spread only within that residual storage equivalent. For example, if the residual saturation capacity of the soil were uniformly 10 % and the porosity 40 %, 100 gal  $(378.5 \text{ L})$  of LNAPL would be contained within 335 ft<sup>3</sup> (9.5 m<sup>3</sup>) of soil (residual saturation is not a uniform parameter). At the beginning of an LNAPL release, both the effective conductivity toward LNAPL and the gradient driving the release dissipate once the release has stopped. Two screening methods of evaluating LNAPL body stability are provided in X3.2.3.1 and X3.2.3.2. The first is based on direct field observations; the second is based on multiphase theoretical considerations.

X3.2.3.1 *Direct Field Observation—*Observing LNAPL body stability from site data is relatively straightforward once it is recognized that the presence or absence of LNAPL in a well is not a definitive indicator of stability, particularly where there are background groundwater level fluctuations. However, combining LNAPL observations in wells with groundwater concentration history, the stability (or instability) of the LNAPL body can be directly observed. This is the case if there are any chemical compounds in the LNAPL that are soluble in groundwater. The inspection of the data history can be completed through simple time-series mapping or more advanced geostatistical evaluations (see Tier 1 site example in [Appendix](#page-42-0) [X6\)](#page-42-0). The user should review the data sets to identify the dissolved-phase plume and the stability of the center of mass of that dissolved-phase plume. If the dissolved-phase plume is stable then, by implication, so generally is the LNAPL body. Since a dissolved-phase plume that results from an LNAPL body is present regardless of whether LNAPL is observed in wells, groundwater concentration patterns provide a direct indication of stability or mobility. This analysis can be coupled with LNAPL observations in wells to determine whether the maximum extent of the LNAPL body is expanding. Given that <span id="page-33-0"></span>many sites have a database of historic groundwater and LNAPL elevation measurements and groundwater concentration records, this is the favored method of stability evaluation because it is based on direct observation and available data and information.

X3.2.3.2 *Multiphase Estimates of LNAPL Stability—*If it is assumed that a steady-state approximation might hold, then Darcy's law can be applied to derive the Darcy flux (specific discharge  $= q_n$ ) and the average LNAPL velocity (seepage velocity =  $V_n$ ). The variables in the Darcy equations can be derived by several methods.

$$
q_n = -k_r k_{ij} \frac{\rho g}{\mu} i_n = -K_n \cdot i_n \tag{X3.7}
$$

$$
V_n = -\frac{k_r k_{ij} \frac{\rho g}{\mu} i_n}{\Theta_{en}} = -\frac{K_n \cdot i_n}{\Theta_{en}}
$$
(X3.8)

*(1)* The LNAPL gradient is estimated based on LNAPL elevations in a calculation that is directly analogous to the calculations for groundwater gradient determination (see Bedient et al, 1999 **(11)**). However, because of variations in the LNAPL body, it is often useful to consider a three-point analysis of wells in close proximity to an area of interest, while a groundwater gradient determination might be based on more widely spaced groundwater elevation measurements.

*(2)* The LNAPL hydraulic conductivity can be measured directly through analysis of LNAPL pump testing or baildown testing (for example, see Huntley 2000 **[\(12\)](#page-67-0)**).

 $(3)$  Intrinsic permeability  $(k_{ii})$  can be measured in the laboratory from soil cores or derived from the hydraulic conductivity to water if known through aquifer testing.

*(4)* The relative permeability can be measured in the laboratory from soil cores or estimated through empirical relationships to LNAPL saturation. A simple approximation of relative oil permeability is  $k_r = S_o^2$  (Charbeneau et al, 1999 **(13)**). For either estimate, the user needs to know the saturation or saturation profile of LNAPL in the subsurface for both the relative permeability and for the effective LNAPL porosity (Θ*en*).

*(5)* Combining these terms results in the potential Darcy flux and seepage velocity. Note that the forces that impede LNAPL body movement at its periphery are not considered, which results in a calculated velocity potential that is not in fact evident in the field. This analysis by itself, without careful consideration of other field observations, can be misleading. It is recommended that a lower limit to velocity potential be used as a screening value; for instance, landfill liners may have allowable seepage potentials of  $1 \times 10^{-6}$  cm/s. Regardless of the specific lower limit for the velocity potential, site-specific results greater than the screening value would typically result in additional data evaluation, collection, or analyses (for example, moving to a higher tier LCSM).

*(6)* Screening analyses similar to those above can be used to derive estimates of LNAPL recovery through hydraulic means (Charbeneau et al, 1999 **[\(13\)](#page-67-0)**; Charbeneau 2003 **[\(14\)](#page-67-0)** ) within similar limitations.

X3.2.4 *Estimating LNAPL Chemistry Through Groundwater Concentrations—*Often, there is a relatively large historic database of groundwater concentration results. Monitoring wells in or near the LNAPL body can be used to approximate the chemical composition in the LNAPL. Raoult's law indicates that the effective solubility of any compound in a multicomponent LNAPL will be equal to the product of its pure phase solubility and its mole fraction in the LNAPL (the dissolved-phase concentrations are relatively insensitive to LNAPL saturation until they reach very small values) (see Charbeneau 2000 **[\(15\)](#page-67-0)** and Bedient et al, 1999 **[\(11\)](#page-67-0)** for additional information). Based on the effective dissolved-phase concentration in groundwater in the source zone, the user can estimate the mole fraction of that compound in the LNAPL. For instance, if benzene in the source zone is detected at 17 500  $\mu$ g/L, and its pure phase solubility is 1 750 000  $\mu$ g/L, then the approximate mole fraction in the LNAPL is 1 %. These approximations are useful when direct measurements of LNAPL chemistry are unavailable. However, factors such as dilution, ion activity, non-ideal LNAPL partitioning, and others can affect this approximation.

X3.2.5 *Estimating Chemical Flux in the Soil Vapor and Groundwater Dissolved Phases—*The soil vapor and dissolved fluxes are estimated by combining concentrations of chemicals of concern in the LNAPL, hydrogeologic conditions, and the LNAPL body dimensions. There are many methods of estimating fluxes, and this brief discussion is intended to assist the user in getting started and understanding some basic concepts. Calculation tools are available to assist in these estimates (for example, Huntley and Beckett 2002 **(2)** ).

X3.2.5.1 *Groundwater Flux—*The groundwater system receives dissolved-phase chemicals from the LNAPL body. The first step is to calculate the effective solubility of any chemical of concern. Based on the LNAPL geometry, the user can conservatively estimate a planar, vertical area orthogonal to groundwater flow that encompasses the transmission zone. The mathematical product of the groundwater Darcy velocity and the effective solubility gives the local area mass flux. Eq X3.9 shows the simple form of groundwater flux described here, and the more rigorous form in Eq  $X3.10$  that recognizes flux (*J*) is a function of a variable concentration profile (integral of both *C*, concentration, and  $q_{gw}$ , the groundwater flow). Multiplying the flux by the planar area of interest gives the total mass discharge. Because the simple estimate ignores transverse vertical dispersion below the LNAPL body, the user should overestimate the size of the plane across which mass is moving or, more rigorously, directly estimate and integrate the vertical dispersive flux term. Quantitative tools developed by the API perform these analyses (Huntley and Beckett 2002 **[\(2\)](#page-67-0)**).

$$
J_{\rm gw} = q_{\rm gw} C_i \tag{X3.9}
$$

$$
J_{\rm gw} = \int_{-\infty} q_{\rm gw} C(z) dz \tag{X3.10}
$$

*(1)* If a site is well characterized, the user can inspect dissolved-phase concentrations at down-gradient locations and

 $\infty$ 

<span id="page-34-0"></span>estimate the flux from those direct observations. Because of plume dispersion and a host of other transport factors, the user would expect the plane across which mass is moving at the down-gradient location to be larger than at the LNAPL body where fluxes are beginning (see [Fig. 5](#page-8-0) in this guide). If a chemical of concern is not being transformed or degraded (conservative solute), and a groundwater dissolved plume is at steady state, then the total mass discharge is equal at all locations. If mass discharge is decreasing across sequentially increasing distances, it implies transformation or degradation processes are at work. As discussed in Section [7](#page-14-0) of this guide, the points at which flux or concentration target levels are applicable and the point in time at which the measurements and comparisons to target levels are made are defined during the decision process.

*(2)* Groundwater transport can be estimated using many different modeling methods, including those outlined in the RBCA process (Guide [E1739\)](#page-40-0).

X3.2.5.2 *Vapor Flux—*In a fashion similar to the process for estimating groundwater flux, vapor flux can be estimated by some simple approximations that combine the estimated concentrations of chemicals of concern in the LNAPL with soil properties affecting vapor transport. Eq X3.11-X3.13 show the relationship between the effective vapor concentration  $(C_{veff})$ and vapor flux.

*(1)* Eq X3.11 is the ideal gas law:

$$
C_{\text{veff}} = \frac{X_m V P_m M W_m}{RT}
$$
 (X3.11)

where:

 $X_m$  = mole fraction of compound *m*,<br> $VP_m$  = pure phase vapor pressure of the  $VP_m$  = pure phase vapor pressure of the compound,  $MW_{m}$  = molecular weight,  $MW<sub>m</sub>$  = molecular weight,<br> $R$  = ideal gas constant.  $R$  = ideal gas constant, and  $T$  = temperature all in cons  $=$  temperature, all in consistent units. *(2)* Eq X3.12 is Fick's First Law:

$$
J_{\nu} = E_{\nu} D_e \frac{dC_{\nu eff}}{dZ}
$$
 (X3.12)

where:

 $J_{\nu}$  = vapor flux,

 $E_v$  = flux partitioning efficiency factor, and

*De* = effective vapor diffusion coefficient.

*(3)* Eq X3.13 is the equation for the effective diffusion coefficient:

$$
D_e = D_a \frac{\Theta_a^{3.33}}{\Theta_t^2}
$$
 (X3.13)

where:

- $D_a$  = free air diffusion coefficient,
- $\theta_a$  = air-filled porosity, and
- $\theta_t$  = total porosity in the vadose zone.

*(4)* As with the groundwater estimate, the calculation area is orthogonal to the direction of transport, which for vapor, is assumed to be upward (see [Fig. 5](#page-8-0) of this guide). The area of mass transfer would be related to the LNAPL body footprint, that is the plan view.

#### Geology Can Greatly Affect Flux & Timing



(Beckett 2004, (Ref **[16](#page-35-0)**))

NOTE 1—For the same receptor, the compounds with greatest combined flux and toxicity generally present the greatest potential near-term risk (to scale).

#### **FIG. X3.2 The User Can Immediately See that the Flux Magnitude for a Compound Like MTBE is Many Orders of Magnitude Greater than the Flux Potential for Xylenes or Fluorene**

*(5)* As with groundwater flow, the user could estimate mass flux and total mass discharge at any location above the LNAPL body. Its mass would be constant for a conservative vapor phase compound and diminish where transformation or degradation processes affect the vapor phase compounds.

*(6)* Unlike groundwater flow, this vapor-partitioning estimate has no advective component and is driven only by the chemical gradient. Where advective vapor movement is present, this simple approximation will potentially underestimate flux, and other more advanced modeling or analysis methods may be warranted. This may require a Tier 2 or Tier 3 LCSM.

X3.2.6 *LNAPL Flux Implications—*As stated in the main body of this guide, LNAPL is the controlling chemical source term for as long as it is present in the formation. Because of many interrelated factors, it is useful to discuss the dynamics of LNAPL depletion in terms of source mass, composition, and geologic conditions controlling ambient movement of groundwater and soil vapor.

X3.2.6.1 For the same LNAPL source mass in differing geologic settings, the earth materials and their effect on the propagation of chemicals varies significantly as a function of the natural variability in earth material properties. All other things being equal, the user can see that the flux from clayey materials is thousands of times less than flux from clean sand materials (see Fig. X3.2). These estimates are sensitive to groundwater conductivity, effective diffusion coefficients in the vadose zone, and capillary effects.

X3.2.6.2 Similarly, for the same initial chemical mass in place, the time to reach some target flux or concentration also varies with those same properties. Fig. X3.2 shows that for the same initial mass, fine-grained materials will require significantly longer periods to reach some *de minimis* flux or concentration level.

<span id="page-35-0"></span>

(Beckett 2004, (Ref **[16](#page-67-0)**))

NOTE 1—More vapor and groundwater flux is evident in coarse materials, and similarly, the time to reach a *de minimis* concentration in the LNAPL is shorter (to scale).

#### **FIG. X3.3 Relative Fluxes for Benzene at a Point in Time for Different Soil Types that Are Found at Various Sites**

X3.2.6.3 The chemicals within the LNAPL and their inherent properties like mole fraction, solubility, volatility, and others also have a strong effect on the expected fluxes emanating from the LNAPL source. Fig. X3.3 shows how those chemical properties affect the flux at a given point in time, with soluble and volatile compounds like MTBE having a high flux potential, and low solubility materials like fluorene having *de minimis* flux, all other things being equal.

X3.2.6.4 A finite LNAPL body obviously contains a finite mass of the various chemical compounds that make up the original LNAPL released to the environment. Given the flux attributes in  $X3.2.6.1 - X3.2.6.3$ , it is also useful to consider how individual compounds may partition through time from the LNAPL source. Fig. X3.4 shows how different compounds partition through time, with the left axis showing the relative concentration and the bottom axis showing relative time. The less soluble/volatile compounds actually increase in mole fraction through the partitioning process, and short-term increases in their relative concentrations are expected. The degree to which this happens depends on the solubility/ volatility contrasts between the light- and heavy-end compounds in the LNAPL. Fig. X3.5 gives a relative comparison of the relative benzene lifespan for large and small releases under high- and low-flux conditions.

X3.3 In summary, many attributes of the LCSM can be described using existing site data and various aspects of the



NOTE 1—In this case, aromatics and MTBE in gasoline are considered. **FIG. X3.4 For the Same Hydrogeologic Conditions, the Relative Longevity in the LNAPL Source Varies with Chemical Properties for the Compounds of Interest**





**FIG. X3.5 The Potential Longevity of Benzene in the LNAPL Source, Measured as Concentrations in Groundwater, for Large and**

**Small Releases Under High and Low Flux Conditions**

associated physical and chemical relationships. Relatively simple calculation techniques have been provided in this appendix to assist the user in getting started. In the end, some level of quantification is required for risk-based analyses and remedial selection evaluations.

#### **X4. DATA COLLECTION CONSIDERATIONS AND RESOURCES**

<span id="page-36-0"></span>X4.1 *Introduction*—The following sections provide information on data collection that may be useful when developing an LCSM or when filling data gaps.

X4.1.1 Historic environmental data collection for groundwater issues has generally focused on chemical concentrations in soil and groundwater, with qualitative descriptions of soil and physical properties. These "standard" data results are outcomes of the underlying multiphase and transport parameters of the subsurface and release system. As noted in [Appendix X2,](#page-25-0) a variety of parametric controls influence multiphase plume migration, risk and flux in primary and secondary phases, and potential LNAPL remediation approaches. So, "standard" data should be used in conjunction with other parameter needs in developing the LCSM.

X4.2 *Scope*—This appendix provides an overview of direct and indirect data collection methods that can be used to assist in building a Tier 1 LCSM, or in collecting additional data when upgrading to a Tier 2 or Tier 3 LCSM. Data collection is needed when common site data are insufficient for decisionmaking.

X4.3 [Table X4.1](#page-37-0) and the following subsections discuss different advanced LCSM delineation methods. "Advanced methods" refer to those that are different from standard drilling and sampling of soils, monitoring well gauging, and sampling of groundwater. These methods are helpful in gaining significant insight into the plume conditions forming the basis of the LCSM. In the area of geophysical methods, the discussion is limited to those tools that to date have been found most useful toward building a Tier 2 or Tier 3 LCSM.

X4.4 The relative expense and limitations of multiphase data collection and testing on a discrete basis suggests that interpretation of broader screening techniques may be useful in maximizing the benefit of sparse and expensive pointmeasurement data. Pairing these point data with broader and less-expensive screening information can allow cost-effective development of the LCSM. For instance, using the laserinduced fluorescence geophysical method (LIF, which will be discussed subsequently) paired with more advanced multiphase parameters can extend those advanced parameters across a larger spatial domain.

X4.5 Fractures and secondary permeability features in rock, clays, or other materials and settings are a subset of potential conditions that often warrant a different conceptualization and degree of characterization and understanding. Often, fractures and secondary permeability features act as conduits for LNAPL movement and enhance the lateral and vertical movement during the spreading phases of the plume. The interstitial matrix material can act as a chemical sink for LNAPL or dissolved-phase compounds. Where such features are present, complex LNAPL conditions and plume distributions are often expected. LNAPL can travel farther, faster, and impact a greater volume of soil and rock materials than would generally be expected in a soil porous medium. The user is directed to [Appendix X1](#page-18-0) for additional references on fractured materials and hydrogeologic analyses.

X4.6 The objectives of the advanced data collection tools are to better define the range of values for one or more of the critical LCSM elements, including:

X4.6.1 Lateral and vertical distributions of the LNAPL body and its associated plumes in soil, groundwater, and vapor phases;

X4.6.2 Definition of soil and liquid physical properties controlling distribution, mobility, flux, and remediation;

X4.6.3 Characterization of the distributed chemical composition of the plume, chemicals of concern, and other attributes that affect flux, risk, and remedial action; and

X4.6.4 Identification of geologic heterogeneity, secondary structural features, and other facets of the subsurface structure that affect transport, flux, risk, and remedial action.

X4.7 *Delineation and Parameter Determination*—Several categories of potential delineation methods are provided in [Table X4.1,](#page-37-0) including several individual methods that will not be explicitly discussed in this text. The table is not comprehensive, but includes commonly available techniques for building a more robust LCSM as of the time of this guide preparation.

X4.7.1 The following sections discuss a subset of specific advanced investigation methods that have been found useful in building Tier 2 or Tier 3 LCSM. These methods can provide a much richer data density than standard media sampling on a limited interval basis, particularly when integrated with that existing information. Experience suggests that acquiring spatially dense data, vertical or lateral, is important to higher levels of LCSM understanding (see the Tier 2 example in [Appendix X5\)](#page-40-0).

X4.7.2 As with all characterization methods, applicability will vary with geologic and chemical conditions, and it is important to consider those expected conditions before selecting the most appropriate characterization methods. These methods are typically combined with existing site knowledge and information to lead to comprehensive use of all available site data applicable to the LCSM.

X4.8 The following delineation methods are most applicable to assessing lithologic distributions, although several have crossover attributes related to the presence of LNAPL. Most methods produce non-unique results, meaning that interpretation is needed to resolve the results, or use of more than one method may be helpful. For this reason, the greatest utility is often gained when correlating the results of these delineation methods to continuous geologic cores from the subject site for the purposes of calibration and refining the interpretation of the results.

#### **TABLE X4.1 Data Collection Methods**

<span id="page-37-0"></span>

1. Release source(s) & timing

2. Geometry of the LNAPL body

3. LNAPL physical characteristics

4. LNAPL chemical characteristics

5. Groundwater and hydrogeologic conditions

5a. Properties and distribution of soil and rock materials

5b. Groundwater flow & gradient conditions

6. Receptors, location, characteristics

7. Flux; LNAPL, Groundwater, Vapor, other

X4.8.1 *Cone Penetrometer (CPT)—*A hydraulically driven tool that collects the tip and sleeve resistance of the soil materials to the passing of the tool. Some variants also collect pore pressure and pore pressure dissipation data. The tip and sleeve resistance, and other factors, often indicate the variation in lithologic materials.

X4.8.2 *Resistivity/Electrical Conductivity—*Geologic materials, and many LNAPLs, have geoelectric properties that vary and can be used to characterize those materials. Surface and down hole methods are available to measure resistively or electrical conductivity. It is useful to calibrate these readings to a few continuous cores from a site to ensure proper interpretation of the results. These methods are often very efficient, but require knowledge of the physics of the method, along with interpretive skills in data analysis. These tools can be employed down non-metallic cased holes, as well as open boreholes (often mud filled).

X4.8.3 *Down-Hole Gamma Logging—*This method can also assist in delineation of lithologic units using equipment that is similar to the downhole resistivity/conductivity logging discussed in [X4.8.2.](#page-37-0) Gamma logging measures the radioactive decay emissions of the earth materials (primarily potassium-40 and uranium daughter products), and can often be used to distinguish between sands and finer-grained materials. It is useful to interpret gamma and EM log simultaneously for the best understanding of lithologic distributions. This tool can be employed in cased holes, as well as open boreholes (often mud filled).

X4.8.4 *Other Survey Techniques—*Refraction/reflection surveys, ground penetrating radar, self-potential, and some other geophysical techniques can also assist in determining bedding horizons, faults, and other geologic features. Very low frequency (VLF) radio signals can often assist in determining the orientation and location of significant fracture systems. This grouping of geophysical methods and others are at the current time more costly to apply and require significant interpretation. While they have utility in certain environments, the user should be aware of limitations and select a method that is appropriate for the application.

X4.9 The following methods pertain primarily to chemicals of concern and LNAPL delineation, with some geologic crossover.

X4.9.1 *Induced Fluorescence—*Laser and ultraviolet induced fluorescence (LIF, UVIF) take advantage of the propensity of many compounds in petroleum LNAPL to fluoresce when excited by certain wavelengths of light. The tools beam a light pulse (UV or laser) into the geologic formation through an optical window in the tool. The subsurface fluorescence response is returned by fiber optic cable and can be used to indicate the presence and sometimes the magnitude of LNAPL impacts. LIF also returns waveform information that can be used to evaluate, to a limited degree, chemical variability in the LNAPL. These tools are efficient and can collect dense data sets in a short timeframe, and are often hydraulically driven into the subsurface simultaneously with CPT investigations (discussed above), combining two useful datasets in a single investigation event.

X4.9.2 *Membrane Interface Probe—*The permeable membrane interface probe (MIP) is another downhole tool that has both geophysical and analytic chemical detectors. The MIP generates chemical readings for volatile compounds by heating the soil materials and collecting volatized gasses through the membrane for subsequent chemical analysis. The MIP geophysical tool measures the apparent electrical conductivity of the formation materials, which can be used to interpret geologic distributions.

X4.9.3 *Direct Push Soil/Groundwater Sampling—*In many settings, discrete soil or groundwater samples can be collected using direct push hydraulic methods, potentially augmented with an onsite mobile analytical laboratory. Vertical and lateral sampling density can be high in amenable conditions, and assist in delineation of the LNAPL body, its chemistry, and the earth materials in which the LNAPL body resides. Sparse sampling, however, is of limited use for multiphase characterization, so the appropriate density should be considered, with decisions generally assisted by real-time field data mapping.

X4.9.4 *Electrical Resistivity Mapping—*Surface mapping of electrical resistivity or conductivity can generate anomaly maps of interpretive utility. For instance, low electrical resistivity might be associated with high-localized total dissolved solids (TDS) in groundwater. The user would similarly expect patterns of higher resistivity around LNAPL bodies, all other things being equal. Surface geophysical mapping of groundwater plumes works best in shallow conditions and where man-made artifacts affecting electromagnetic signals have a limited presence. Because of the sensitivity to these artifacts, these surface geophysical methods tend to have limited applicability except under ideal circumstances.

X4.9.5 *Evaluation of LNAPL Remediation Results—* Remediation results are direct and indirect indicators of the subsurface conditions affecting that response. Irrespective of the methods applied (hydraulic, chemical, or other), key items pertaining to the LCSM are often discernible. For instance, the rate of decay of hydraulic LNAPL recovery says something about the conditions of the LNAPL remaining and its diminished mobility and recoverability. A remedial action that recovers mass, but has no effect on the concentrations in groundwater or soil-vapor plumes, suggests that some portion of the LNAPL body remains in place and was likely untreated by that action. Changes in groundwater chemistry and mole fractions of chemicals of concern can also be a direct indicator of LNAPL conditions in the subsurface. Generally, the more detailed and discrete the remediation data, the better the interpretive capacity. Annual total bulk fluid recovery data from a multi-well remediation system is less valuable than tracking of individual locations at sufficient time density. Since the goal of remedial actions is to have a direct and demonstrable benefit, more detailed data tracking can also serve to assess the degree to which remediation metrics are achieved and determine when the system has reached the end of its effectiveness.

X4.10 *Coring and Laboratory Testing* —The delineation methods above, or existing information and plume mapping, can assist in identifying areas where continuous-coring of earth materials can greatly assist in delineation and LCSM understanding. Cores are real physical examples of the earth materials and LNAPL impacts, and are an irreplaceable component of most advanced characterization activities.

X4.10.1 *LNAPL Confirmation Techniques—*There are a number of methods that might be used to directly confirm the presence of LNAPL in soil core samples. Field tests can include agitation of a soil sample in a jar of clean water, allowing it to settle, and inspecting the upper surface for LNAPL sheens or emulsification. Similarly, a paint filter test is



<span id="page-39-0"></span>sometimes used where a soil sample is placed in a filter funnel, water is added, and the filter is examined for separate phases. Slightly more advanced methods include reactive dye tests, such as Sudan Red (IV). Use of an ultraviolet lamp of a wavelength of approximately 3600 Å (long wave) can be used to fluoresce many petroleum hydrocarbons using a dark box (depending on LNAPL composition). Field mobile laboratories are another option. Regardless of the methods used, confirmation of the presence of LNAPL in soil can be an important part of the LCSM.

X4.10.2 *Photographic Logging—*Developing a photographic record of cores under ambient and ultraviolet light provides a data-rich and permanent documentation of the earth materials and LNAPL impacts encountered in the core materials. Written visual descriptions, regardless of the quality of geologic logging, fall well short of the information conveyed in field or laboratory photo logging. Photo logs can be set to vertical scale with geophysical logs to improve interpretations about the distribution of earth materials and LNAPL impacts.

X4.10.3 *Laboratory Samples—*Sub-samples of continuously cored earth materials may be sent to a chemical or petrophysical laboratory. A reference for key properties is API Publication 4711 **[\(5\)](#page-67-0)**.

X4.11 *Basic Soil Properties*—Typically the soil properties of interest include porosity, grain and bulk density, native state moisture content, air content, and intrinsic permeability to water. These properties control fluid movement and other aspects of chemical transport and cleanup in subsurface materials.

X4.11.1 Grain-size distributions can correlate to other soil properties, even though grain-size data are not themselves a controlling parameter. Where correlations to permeability, capillarity, residual saturation, or other features exist, grainsize distributions can be used to extend LCSM understanding about parameter distributions.

X4.11.2 Multiphase soil properties are those that control the distribution of multiple fluids in the pore space (phase saturation), and the relative ability of one phase to move in the presence of other fluid phases (for example, oil moving in the presence of pore water).

X4.11.3 Soil capillarity controls saturation/pressure relationships of multiple fluids in porous media and is a key multiphase property. More advanced methods may include evaluation of hysteresis and other more complex factors.

X4.12 *LNAPL Saturation*—As the chemical source term, it is often useful to measure the native state saturation of LNAPL in cores. Saturation and total hydrocarbon analytical measurements can be correlated through soil and LNAPL density terms, as long as the total petroleum hydrocarbons measurement spans the full chromatographic signature of the LNAPL of interest.

X4.13 *Residual LNAPL Saturation* —As the endpoint to hydraulic continuity/movement, the residual LNAPL saturation is an important property of the subsurface materials. This property is strongly dependent on hysteresis, and direct use of laboratory-derived values is sometimes not valid depending on the testing method.

X4.14 *Relative Permeability*—The relative permeability controls movement of LNAPL and other phases as a function of phase saturation. These tests are relatively expensive, and practitioners often rely on pre-determined empirical relationships. While a practical necessity in many cases, these empirical relative permeability relationships do not always hold true.

X4.15 *Intrinsic Permeability to Phases of Interest*—These tests are conducted with fluids of interest frequently collected from the field. It is often observed that intrinsic permeability varies as a function of the testing fluid, presenting challenges in simple multiphase calculations.

X4.16 *Physical Fluid Properties* —The properties of the fluids in the pore space influence their relative ability to move and be present in a multiphase state.

X4.16.1 Fluid viscosity is important to phase movement and recovery, particularly for petroleum products that have significant variability between fuel and oil grades.

X4.16.2 Fluid density is used in capillary relationships, although the range of variability is generally small for petroleum LNAPL. This is not a highly sensitive parameter.

X4.16.3 Interfacial tension between phases is used to scale the capillary relationships above to all phase couplets in the geologic system (air-water, water-oil, oil-air). Because the capillary relationship is nonlinear, the effect of interfacial tension can be significant to estimates of oil volume in-place, mobility, and recoverability.

X4.17 *Chemical Analyses*—Chemical determination can be performed on the LNAPL extracted from cores, even if the saturation is below residual. LNAPL samples can also be collected from wells where it accumulates, but discrete cores present more precise spatial control than does well sampling.

X4.17.1 The specific chemical analytical methods depend on the composition of the parent LNAPL and the questions posed by the site assessment. Typically, chemicals of concern are considered. The user may also consider indicators of weathering, sources of crude oil, refining characteristics, additive content, boiling point range, and others.

X4.17.2 Standard sampling for laboratory analyses of LNAPL in soils is useful when the samples are derived from the smear zone. Sampling should focus on an adequate spatial distribution reflective of the LNAPL body geometry and understanding the core and peripheral body locations in three dimensions. It is useful to request the gas chromatograms (GC) for these samples and the fuel standards used by the laboratory. From the chromatograms, qualitative evaluations may be conducted regarding sample similarities and differences. This information is useful in the development of the LCSM in describing the LNAPL body.

X4.17.3 Advanced chemical evaluations can include several laboratory analytical evaluations that might be performed on LNAPL extracted from soil cores or collected from observation

<span id="page-40-0"></span>wells. These analyses are generally performed to better understand the potential sources of releases, the age of releases, or other differences in composition that can assist in understanding LNAPL body genesis and current chemical conditions. Some categories of advanced chemical characterization are provided below:

X4.17.3.1 C4 to C40 hydrocarbon range "fingerprint" using gas chromatography GC/FID;

X4.17.3.2 C4 to C26 detailed hydrocarbon scan by gas chromatography with GC/FID;

X4.17.3.3 Detailed speciation by mass spectrometry (MS);

X4.17.3.4 Selected biomarker identification;

X4.17.3.5 Organo-lead compounds and total lead;

X4.17.3.6 Sulfur spectrum fingerprinting;

X4.17.3.7 Oxygenate and additive spectrum; and

X4.17.3.8 Isotopic analyses.

#### **X5. REMEDIATION METRICS**

X5.1 *Introduction*—The process of defining quantifiable remediation metrics for any corrective action site can be difficult because the user must consider many objectives and requirements. Whether risk-based remedial actions or non-riskbased remedial actions, or a combination of both, are to be considered, the more specifically the user can define the remediation metrics, the easier it will be to design, implement, and monitor the action. Remediation metrics should be developed to assess the ability of remediation technologies to achieve the applicable regulatory goal at appropriate points of compliance. In addition, with well-defined remediation metrics, the completion of the remediation is more easily demonstrated. Benefit remediation metrics are analogous to performance goals that indicate the objectives have been met. Cost remediation metrics are those associated with the specific remedial action and represent costs in terms of materials, human resources, dollars, and other specific measures of the remedial action.

X5.1.1 The remediation metrics for LNAPL site objectives that are derived from risk-based drivers are more easily defined because the remedial actions taken address flux (concentration), exposure pathway, or receptor characteristics that drive the potential risk. Those types of remedial actions are identified in Guides [E1739](#page-43-0) and [E2081,](#page-2-0) and other risk assessment guidance documents (USEPA 1989, 1991, 1992, 1996, 1997 (Refs **[\(4-20\)](#page-67-0)**).

X5.1.2 Remediation metrics for LNAPL site objectives that are derived from non-risk factors such as aesthetics, practicable recovery requirements, long-term groundwater protection, and non-degradation objectives may be more difficult to specifically define. If the remediation metrics are not quantifiable, the design and monitoring will be more difficult.

X5.2 Scope—This appendix focuses on guidance for creating specificity in remediation metrics. [Appendix X6](#page-42-0) presents two examples that compare remedial action alternatives based on a simple decision matrix. The LCSM is used in the process of considering each remedial action alternative and its viability in meeting the benefit remediation metrics and the LNAPL site objectives. In addition, the LCSM is used in the scoring of each remedial action alternative on the cost remediation metrics in order to compare alternatives.

X5.2.1 Benefits are factors that achieve specific remediation metrics and other associated environmental benefits.

X5.2.2 Costs, as defined in this guide, relate to the life cycle of the remediation program, and can include many attributes such as public safety concerns, ecological concerns, aquifer resource damages, groundwater transfer and disposal, increased human health risks, raw material use, energy use, pollution generated by the remedial action system, business impairment or other factors that are not beneficial to the environment or people. Monetary spending is also a cost factor.

X5.2.3 This appendix does not review specific remediation technologies, but rather focuses on outcomes of implementing those technologies. The user identifies the physical and chemical attributes of a remedial action technology and its affect upon the LNAPL body as described by the LCSM. The user can generate an estimated update to the LCSM from the expected costs and benefits of a remedial alternative. By using the estimated LCSM in comparison to the current LCSM, the expected results of a remedial alternative can be identified. This may be helpful in comparing remedial action alternatives.

X5.2.4 Where interim remedial actions have been taken, the user should consider their affect on the LCSM and update the LCSM accordingly before proceeding in the evaluation of additional remedial actions.

X5.2.5 This guide is flexible in developing the LNAPL site objectives and the benefit remediation metrics, and allows the user to consider local factors, regulatory requirements, and stakeholder goals. The LNAPL site objectives should be identified in as much detail as possible, including the technical or engineering remediation metrics that define the LNAPL site objective. A description of the rationale and benefits for each site objective should also be developed. [Table X5.1](#page-41-0) includes an example of specific LNAPL site objectives.

X5.2.6 For each remedial action alternative, the user identifies the remediation metrics in terms of the benefits and costs. The remediation metrics should identify the ability of the technology to achieve the applicable regulatory endpoint at appropriate points of compliance, in a reasonable time frame. The user also determines the range of attributes used to define the benefits and costs. Each remedial action is scored against the identified remediation metrics. [Table X5.2](#page-41-0) shows benefit remediation metrics for a hydraulic skimming example. In addition, the format of [Table X5.2](#page-41-0) can be used for a simple, scoring system to compare various remedial actions. [Table](#page-42-0) [X5.3](#page-42-0) shows remedial actions and costs for the same hydraulic skimming example. The examples in [Appendix X6](#page-42-0) illustrate the use of this table.

X5.2.7 *Precautionary Statements:*

#### **TABLE X5.1 Example LNAPL Site Objectives and Benefit Remediation Metrics**

<span id="page-41-0"></span>NOTE 1—The example LNAPL site objectives and remediation metrics are provided for illustration purposes only. They are not intended to be directly applicable to any specific site. The user should define the LNAPL site objectives and remediation metrics based on the site conditions, LCSM, and applicable regulatory and other requirements.



†Editorially corrected.

#### **TABLE X5.2 Example Benefits and Costs Scoring**

NOTE 1—In this example, the highest possible benefit score for a remedial action would be 15, relative to other remedial actions for a site, the benefit score of 3 is likely to be a low benefit score; a remedial action with a higher benefit score would be more desirable. For more details of comparing options, see the examples in [Appendix X6.](#page-42-0)



X5.2.7.1 This guide does not advocate specific LNAPL remedial action technologies and may be applied in a sitespecific manner that is consistent with applicable local, state, and federal regulatory guidance and legislation on LNAPL cleanup matters. The site-specific application should consider which chemicals of concern, what site conditions, including the characteristics of the LNAPL body, are important to the selection of remedial action alternatives.

X5.2.7.2 This guide is not a detailed procedure for engineering analysis and design of remedial action systems. It is intended to be used by qualified professionals to develop a remediation strategy that is based on the scientific and technical information contained in the LCSM. The remediation strategy should be consistent with the site objectives. Supporting engineering analysis and design should be conducted in

#### **TABLE X5.3 Example Remedial Actions and Costs**

<span id="page-42-0"></span>NOTE 1—Highest possible cost score for a remedial action would be 15, relative to other remedial actions for a site, the cost score of 10 may be an option with a low cost score. For more details of comparing options, see the examples in Appendix X6.



accordance with relevant professional engineering standards, codes, and requirements.

X5.2.8 This guide is intended to assist the user in determining LNAPL remediation that is effective and efficient at a specific site. Since "effective" and "efficient" are subjective terms, the user must identify the specific remediation metrics that pertain to the LNAPL site objectives and the evaluated remedial actions. The timeframe in which changes can be measured and in which the remedial action is expected to achieve the LNAPL site objectives is an important consideration in determining effectiveness and efficiency.

X5.3 *Procedure*—The procedure for development of LNAPL site objectives from Section [7](#page-14-0) of this guide is discussed in this section, with an emphasis on benefit and cost remediation metrics.

X5.3.1 On a blank version of [Table X5.1,](#page-41-0) the user begins by listing the specific LNAPL site objectives for LNAPL remediation; these are the required or preferred objectives for the remedial action(s). In the second column, the user lists the benefit remediation metrics for each site objective. In the third column, the user outlines the rationale and expected benefits associated with the objective.

X5.3.2 On blank versions of [Tables X5.2 and X5.3,](#page-41-0) the user lists the potential benefits and costs of each proposed remedial action, along with the key elements supporting that determination. Each factor may be weighted in importance (relative to

the other factors) as determined by the user, but such weighting should be specific and applied across all of the alternatives. In the examples in Appendix  $X_0$ , a scoring system of 0 to 3 is used, with 3 being the highest (benefit or cost). The scales (0 to 3) for benefits and costs are not directly comparable.

X5.3.3 The user considers only the benefits of the remedial action and determines if those meet the site objectives, within the timeframes determined to be acceptable for the site, as listed initially in [Table X5.1.](#page-41-0) If they do not, the remedial action is no longer considered viable.

X5.3.4 For potentially viable remedial actions that meet the LNAPL site objectives, the user compares the benefits and costs in a side-by-side scoring exercise, as shown in the examples in Appendix X6.

X5.3.5 Where costs outweigh the benefits, the specific action would generally be deemed ineffective unless specific costs could be reduced by revising the remedial action alternative. A change in a remedial action alternative would cause an update to the initial evaluation in [Table X5.1.](#page-41-0)

X5.3.6 The user repeats this process for all considered remedial action alternatives. The user then compares the remedial action alternatives that meet the LNAPL site objectives to determine the most viable option. This procedure is expected to be iterative for most sites and carried out with input from the stakeholders.

#### **X6. EXAMPLE USE OF THE LNAPL GUIDE**

X6.1 Introduction—The following sections illustrate use of the LNAPL guide as applied to two hypothetical sites. The example sites are developed based on data and information from real sites, but aspects have been simplified for presentation and discussion purposes. In addition, the site information for each of the two examples has been generalized to protect the privacy of the site owners and stakeholders. As discussed in the body of this guide, the risk-based and remediation decisions for any site depend on both the site conditions and the regulatory framework. The example decision outcomes provided below are relevant only for those conditions and, for the same site setting, different decisions could be reached if different risk-based drivers and non-risk factors existed.

X6.2 Purpose—This appendix is intended to illustrate the procedure of building an LCSM of sufficient detail and accuracy so that decisions can be made by the user and the stakeholders. The format of the examples in this appendix generally follows the procedure outlined in Section [7](#page-14-0) of this guide. For simplicity in development and presentation of the examples, information may not be presented to address every aspect included in this guide.

X6.3 Precautionary Statement—Because these sites are hypothetical, they may not fully address all aspects of a real site, or of the LNAPL guide. If there are differences between this material and the LNAPL guide, the LNAPL guide should

<span id="page-43-0"></span>be considered authoritative. These examples are presented only for further information, are not mandatory, and are not intended to modify the information presented in the LNAPL guide.

X6.4 Example 1—This is an example of a hypothetical Tier 1 LCSM site. It is based on a real site in which standard environmental data are sufficient for conservative decisions to be made regarding the risk evaluation and LNAPL body remedial action. LNAPL, while present, was not recognized in the original assessment because accumulations in monitoring wells were not observed. The example has been abbreviated and only key information is discussed.

X6.4.1 *Scenario—*A diesel release occurred at a former truck fueling location as evidenced by laboratory analytical results from soil and ground water samples. The apparent cause of the release was overfilling of the former underground storage tank (UST) and subsequent movement of the released diesel fuel in the subsurface. The site example is developed generally following the procedures section of this guide. A detailed understanding of many of this guide elements for the site is not required to make decisions for this specific case. This is consistent with the Guide [E1739](#page-49-0) process in which only information relevant to the evaluation and decisions is necessary.

X6.4.2 *Site Characterization Information—*This former trucking fuel facility operated from 1960 through 1995, when it ceased operations. It remains vacant to date. However, the land is slated for near-term redevelopment as an office building with no further fuel or chemical storage and dispensing.

X6.4.2.1 The site has been characterized through a series of standard investigations including installation and sampling of soil borings, ground water monitoring wells, and UST removal and associated sampling.

X6.4.2.2 Soil analytical results for total petroleum hydrocarbons in the diesel range were detected in soil at a maximum total petroleum hydrocarbon-diesel (TPH $_d$ ) concentration of 5000 mg/kg in the vicinity of the UST excavation. Soil impacts were defined by several borings and soil samples in the vicinity of the UST excavation (see [Fig. X6.1\)](#page-44-0). The sulfur content in the diesel fuel indicates an older diesel release.

#### **TABLE X6.1 Historical Maximum Concentrations in Soil and Groundwater**



X6.4.2.3 The ground water monitoring history spans 15 years. Ground water dissolved-phase concentrations of diesel range compounds of interest are provided in Table X6.1. Review of the dissolved-phase concentrations through time

**TABLE X6.2 LNAPL Indicators Truck Refueling Location**

Measures	Yes/No
1. Known LNAPL release	No
2. Observed LNAPL (for example, in wells or other	No
discharges)	
3. Visible LNAPL or other direct indicator in samples	No.
4. Fluorescence response in LNAPL range	<b>NA</b>
5. Near effective solubility or volatility limits in dissolved	Yes
or vapor phases	
6. Dissolved plume persistence and center-of-mass	Yes
stability	
7. TPH concentrations in soil or groundwater indicative	Yes
of LNAPL presence	
8. Organic vapor analyzer (OVA) and other field	No
observations	
9. Field screening tests positive (for example, paint filter	<b>NA</b>
test, dye test, shake test)	

shows a stable to decreasing ground water dissolved plume and diminishing mass of chemicals of concern in ground water (see [Fig. X6.2\)](#page-45-0). LNAPL accumulations in wells have not been observed over the history of the monitoring.

X6.4.2.4 Ground water is designated by the state regulatory agency as non-beneficial in this area because of high total dissolved solids content, and there is no current or likely future use of the ground water for potable water supply.

X6.4.2.5 Ground water is present approximately 10 ft (3 m) below grade (fbg), with a hydraulic gradient of 0.005 directed to the west. Site data and USGS regional records indicate that water levels vary over a range of about 5 ft (1.5 m) as a result of seasonal variations in the ground water basin.

X6.4.2.6 Testing indicates the hydraulic conductivity of the aquifer ranges from 0.8 to 26 ft/day (0.2 to 8 m/day), with a geometric mean value of 3.6 ft/day (1.1 m/day). The soil materials vary from sand to silty sand, with relatively distinct bedding of variable continuity. An inter-tidal bay is present about 1500 ft west of the site (down gradient).

X6.4.2.7 No remediation activities have been undertaken at the site, except some removal of localized soil impacts during the UST removal. Access to the site and soil impacts currently exist, but would be restricted or unavailable after construction of the proposed office building.

X6.4.3 *LNAPL Guide Procedure—*The steps of the LCSM development for this site generally follow the procedure in Section [7](#page-14-0) of this guide and are as follows:

X6.4.3.1 Determine if LNAPL is present in the subsurface beneath the site (see [7.2\)](#page-14-0). Table X6.2 shows there are several indicators that suggest probable presence of residual diesel fuel in the subsurface.

X6.4.3.2 Develop the LCSM. The Tier 1 LCSM was developed based on the available information. The specific information needed for the LCSM is presented in [6.6](#page-13-0) in this guide.

*(1)* Define the top, bottom, and lateral distribution of the LNAPL body (see [6.6.2\)](#page-13-0). [Fig. X6.3](#page-46-0) shows the top, bottom, and lateral dimensions estimated from the combined sets of site information.

*(a)* The top of the LNAPL body is defined by the bottom of the UST excavation in which the release occurred.

<span id="page-44-0"></span>

FIG. X6.1 Site Plan **FIG. X6.1 Site Plan**

<span id="page-45-0"></span>

<span id="page-46-0"></span>

FIG. X6.3 LNAPL Conceptual Site Model **FIG. X6.3 LNAPL Conceptual Site Model**

Not Drawn to Scale



#### **TABLE X6.3 Example LNAPL Conceptual Site Model Adequacy Checklist Former Truck Refueling Location**

<span id="page-47-0"></span>NOTE 1—The use of the scoring is site- and regulation-specific. As the complexity of the site increases, the benefit of a detailed LCSM increases. This table is designed to help the user identify what level of complexity, or what tier, for the LCSM is likely to be beneficial to the site. See also [Fig. 4.](#page-7-0)

NOTE 2-The factors should be used to develop a weight-of-evidence to suggest the level of complexity for the LCSM. Sites that have a majority of low scores on the factors would likely fall into a Tier 1 LCSM. Sites with mostly low and medium scores on the factors would fall into a Tier 2 LCSM. Sites with mostly medium and high scores would fall into a Tier 3 LCSM.

#### NOTE 3—In this example application the categories that were applicable to the site were used in the checklist.



#### **TABLE X6.4 Risk Based Screening Levels**



#### **TABLE X6.5 Example 1 LNAPL Site Objectives**



*(b)* The bottom of the LNAPL body cannot be defined with available characterization information because sub-watertable soil sampling was not performed. A conservative assumption is that the base of the LNAPL is approximated by the historic low water table level over the course of fuel-dispensing operations (since 1960).

*(c)* The plume lateral dimensions are inferred based on two combined data sets. Soil detections above 500 mg/kg are interpreted to indicate LNAPL presence, and nearby ground water wells exhibiting concentrations near the effective diesel solubility limits of approximately 15 mg/L are suggested to be within the LNAPL body. Wells beyond this area, exhibiting much lower dissolved-phase concentrations, are likely outside the LNAPL body.

*(2)* Define the chemical makeup of the diesel fuel (see [6.6.3\)](#page-13-0). While there are no LNAPL samples analyzed for chemical composition, two data sets are available that allow this estimation. Soil and ground water samples were analyzed by GC-MS, and those analytical results are direct indicators of the compounds present in the LNAPL. In particular, analytical

<span id="page-48-0"></span>

#### **TABLE X6.6 Example 1 Remedial Actions Decision Matrix—Benefits**

#### **TABLE X6.7 Example 1 Remedial Actions Decision Matrix—Costs**

NOTE 1—See conditions of the Tier I example site in [Appendix X6](#page-42-0) for further background.



results from the most impacted samples will generally represent a conservative or worst-case mass fraction distribution of chemicals of concern. [Table X6.1](#page-43-0) shows the analytical results from the sample with the key chemicals of concern being naphthalene, fluorene, and benzo(a)pyrene; based on the soil sample results, the mass fractions of these compounds are estimated as a fraction of the samples containing the greatest  $TPH<sub>d</sub>$  concentrations. Note, while  $TPH$  values are not directly used in the calculations of ground water or vapor-phase fluxes or in the risk assessment, they are useful for purposes like this estimate of mass fractions of chemicals of concern in the LNAPL, as well as approximations of LNAPL saturation and mass.

*(3)* Determine the distribution of LNAPL mass and chemicals of concern (see [6.6.3\)](#page-13-0). Before making this estimate, it is worthwhile to list the known items from the information given:

*(a)* LNAPL is present as residual LNAPL; it has insufficient inherent mobility to enter a monitoring well.

*(b)* LNAPL is a diesel fuel released from the former UST area.

<span id="page-49-0"></span>

**FIG. X6.4 Exposure Pathway Evaluation**

FIG. X6.4 Exposure Pathway Evaluation

Former Truck Refueling Location Somewhere, USA

<span id="page-50-0"></span>*(c)* The maximum measured concentration of LNAPL is 5000 mg/kg in soil.

*(d)* The dissolved- and vapor-phase plumes result from the residual diesel source. The dissolved-phase plume is both geographically stable and losing mass. If the dissolved-phase plume is losing mass and concentration, then so is the LNAPL body.

*(e)* A stable LNAPL body and diminishing mass within the LNAPL body imply natural mass loss mechanisms are at work.

*(f)* Given these facts, the simple Tier 1 LCSM shown in [Fig. X6.3](#page-46-0) is appropriate for the site. The relative value of a higher Tier LCSM is low (see [Table X6.3\)](#page-47-0).

*(4)* Define the physical properties of the soil and rock materials (see [6.6.4](#page-14-0) of this guide). Interbedded sand and silty sand materials are present beneath the site, with hydraulic conductivity ranging between 0.8 and 26 ft/day (0.2 and 8 m/day); with a geometric mean value of 3.6 ft/day (1.1 m/day). The total porosity is expected to be about 35 to 40 %, and the bulk density is about 1.7  $g/cm<sup>3</sup>$  based on literature values and experience in the area. The total organic carbon content of the soil is less than 0.5 % based on samples collected at other sites in this formation and vicinity.

*(5)* Define the exposure pathways and risks (see [6.6.6](#page-14-0) of this guide). For any chemical exposure pathway, there is zero flux at and beyond a zero concentration boundary (flux  $=$  [concentration  $\times$  flow rate]/unit area). Therefore, site data directly indicate that there is no dissolved-phase mass flux and no potential risks anywhere past the historically observed and now contracting dissolved-phase plume boundary. There is no need for chemical transport or other modeling, as the sufficiently characterized plume dimensions directly demonstrate the site flux conditions for this historic range of hydrogeologic conditions. If future hydrogeologic conditions differ from those forming the basis of findings, then modeling or additional data collection may be warranted. Similarly, the sufficiency of characterization information is site-specific, and appropriate care should be taken in making a field-based determination. See [6.6.5](#page-14-0) and [6.6.6](#page-14-0) of this guide.

*(a)* Ground water ingestion within the ground water plume is precluded by poor background water quality, and there are no plans to develop this saline ground water resource.

*(b)* Dermal contact and soil ingestion are not complete exposure pathways as the residual impacts are greater than 10 fbg (3 m), so direct contact by site workers or visitors is not likely.

*(c)* Short-term exposures are possible for construction workers and others if subsurface excavation and construction activities are performed at depths greater than 10 fbg (3 m).

*(d)* Compounds in diesel fuel have relatively low effective volatility, and it is expected that the vapor pathway is not complete. A comparison to risk-based screening levels (RB-SLs) is needed.

*(e)* Given these conditions, the exposure pathway evaluation is given in Fig. X6.4.

X6.4.3.3 Using the RBCA methodology to develop riskbased screening levels (see Guide [E1739](#page-2-0) and [7.6](#page-15-0) of this guide), it is found that concentrations for all example chemicals of concern are below the example RBSLs and that there are no risk-based drivers for the LNAPL site objectives. No remedial action is needed based on the risk evaluation. (Results are shown in [Table X6.4.](#page-47-0))

X6.4.3.4 Evaluate additional cleanup requirements and nonrisk-based factors (see [7.7](#page-15-0) of this guide). The local regulatory agency requires removal of soil with concentrations above a concentration of 1000-mg/kg  $TPH<sub>d</sub>$  for aesthetic reasons, where feasible.

*(1)* The company responsible for the release has an internal policy for properties being sold that remedial action should be implemented where practical. The planned change in land use and construction for commercial buildings allows for shortterm access to the remaining soil impacts. Because of the shallow depth of impacts and near-term accessibility when the site is transitioned to commercial use, onsite excavation and disposal of the excavated soils is feasible. The coincident construction allows for lower excavation costs than would be incurred solely for remediation purposes. However, under different site conditions, such actions may not have been feasible.

*(2)* It is valuable to document the feasibility evaluation that led to the site decisions, as key elements may change under different site conditions, potentially leading to different decisions (see  $7.11 - 7.16$ ).

*(3)* The LNAPL site objectives developed for the site are included in [Table X6.5.](#page-47-0)

*(4)* The decision matrix leading to excavation as a remedial action at this site is presented in [Tables X6.6 and X6.7.](#page-48-0) In the given decision matrix, the option with the highest benefit score and the lowest cost score is the one that is the best option to implement.

X6.5 Example 2—This is an example of a Tier 2 site in which standard environmental data were not sufficient for decisions to be made regarding the risk evaluation and the needed remedial actions. In this example, a more rigorous conceptualization and understanding of the LNAPL impacts was necessary for informed decision-making. The enhanced understanding came from advanced site assessment techniques, petrophysical sampling, and interpretation.

X6.5.1 *Scenario—*An LNAPL release (gasoline and diesel range petroleum products) occurred in late 1999 at a failed valve box location along a pipeline transect in a large tract of agricultural land, as evidenced by its near surface appearance. Emergency pipeline shutdown procedures were performed, and an initial remedial action was then implemented to excavate impacted soils as determined by field screening.

X6.5.2 *Site Characterization Information—*The site was initially characterized through a series of standard investigation activities including installation and sampling of soil borings, ground water monitoring wells, and sampling of soils associated with the initial remedial action.

X6.5.2.1 Twenty-one soil borings (converted to monitoring wells or temporary piezometers) were installed in three separate site assessment phases over two years. The purpose for installing these soil borings was to evaluate and delineate the

<span id="page-51-0"></span>previously identified LNAPL and dissolved-phase hydrocarbons at the site. A general site map, monitoring well locations, and other important features are shown in [Fig. X6.5.](#page-52-0) Additionally, numerous soil samples were selected for laboratory analysis for TPH, poly-nuclear aromatic hydrocarbons (PAH), and benzene, toluene, ethyl benzene and xylenes (BTEX).

X6.5.2.2 Following the initial remedial action excavation, soil analytical results indicated benzene at a maximum concentration of 75.5 mg/kg, toluene at 131 mg/kg, ethyl benzene at 87.8 mg/kg, and xylenes at 191 mg/kg. Maximum analytical results for TPH in the C6-C12 range were 11 800 mg/kg, C12-C21 range was 9450 mg/kg, and C21-C35 was 3300 mg/kg. Soil impacts were measured at several soil borings, but this characterization did not indicate the LNAPL body conditions subsequently observed.

X6.5.2.3 The LNAPL body was mobile in the early stages following the release. This was determined based on new dissolved-phase concentrations of chemicals of concern in ground water followed by the arrival of LNAPL at previously clean monitoring wells. Standard site characterization data were insufficient to evaluate the potential threat posed by the LNAPL movement or to evaluate when movement might cease, and advanced data collection efforts were implemented to enhance the LCSM.

X6.5.2.4 For various reasons, such as the mobile LNAPL body, and difficulty with defining the vertical extent of the impacted zone in the heterogeneous soils encountered using conventional drilling and sampling techniques, a decision was made to perform a cone penetrometer (CPT) and rapid optical screening tool (ROST) assessment using laser-induced fluorescence (LIF). During the CPT/ROST testing event, 26 borings were advanced at locations shown in [Fig. X6.5](#page-52-0) to delineate and characterize the LNAPL body. In addition to this event, a second CPT/ROST event was performed 18 months later to assess the LNAPL mobility that the initial event alone could not detect. [Fig. X6.6](#page-53-0) shows how the LNAPL body enlarged over the initial two years after the release by using the two LIF events and routine LNAPL thickness measurements to map the spread (see [Fig. X6.7\)](#page-54-0). The geophysical results were used to guide soil coring and petrophysical analyses to enhance understanding of the LNAPL body, the potential exposure pathways, and the remedial action options.

*(1)* There was no appreciable enlargement of the LNAPL body beyond the initial two-year spreading period.

*(2)* The observed LNAPL body gradients have diminished by one to two orders of magnitude (see [Fig. X6.8\)](#page-55-0).

*(3)* The observed LNAPL body footprint has experienced a decrease in net spreading from 10 to 50 ft/day (3 to 15 m/day) early in the release to less than 0.1 ft/day (0.03 m/day) (no discernible movement currently; see [Fig. X6.9\)](#page-55-0).

*(4)* Based on the CPT/LIF results, continuous coring of selected locations was implemented in key areas of the LNAPL body. Cores were first photographically logged under ambient and UV light. Based on review of the photo logs, geophysical logs, and other supporting information, sub-samples were selected for basic and advanced petrophysical testing to characterize the lithologic properties controlling the LNAPL body movement and evaluate potential remedial action options.

X6.5.2.5 The ground water gauging history spans four years and includes 29 monitoring wells.

*(1)* Ground water analytical results indicated concentrations of BTEX compounds at maximum detections of 26 200, 19 500, 8370, and 24 300 µg/L, respectively. These sample values are representative of dissolved phase conditions for BTEX in the LNAPL body that are at the effective solubility limits. Most recent time series maps of the ground water dissolved-phase plume show a steady center of mass and a static lateral extent. LNAPL accumulations in monitoring wells have been observed over the history of monitoring and demonstrate an expanding LNAPL body in early time.

*(2)* Ground water is designated as non-beneficial in this area as a result of high total dissolved solids content (greater than 1000 mg/L) and limited well yield (within 150 to 5000 gpd). There is no current or future planned use for the ground water as a water supply. No water wells are located within a 0.5-mile (0.8-km) radius of the site. The nearest surface water body is a lake that is several thousand feet away.

*(3)* Ground water is present approximately 15 to 20 ft (4.6 to 6 m) below grade (fbg), with a hydraulic gradient of 0.03 directed to the southeast. Aquifer testing using slug tests indicated hydraulic conductivity ranges from about 0.1 to 30 ft/day (0.03 to 9 m/day). The soil materials vary from clay to marly silt-clay-sand mixtures with some sandy lenses. The more permeable sand beds and seams are the likely transport mechanism for LNAPL and ground water dissolved-phase plume movement. Vertical LNAPL movement between sandy zones is likely through secondary features in the clayey materials such as fractures, or root bores.

 $X6.5.2.6$  Approximately 7000 yd<sup>3</sup> (5350 m<sup>3</sup>) of soil were excavated in response to the discovery of the release. Corresponding soil sampling indicates that some of the more highly saturated soils have been removed, but impacts remain. In addition to excavation, other initial remedial actions undertaken at the site have included limited hydraulic LNAPL recovery from one well, a dual-phase extraction test, and limited skimming of LNAPL from wells in a trench.

X6.5.3 *LNAPL Guide Procedure—*The steps of the LCSM development for this site generally follow the procedure in Section [7](#page-14-0) of this guide and are as follows:

X6.5.3.1 Determine if NAPL is present in the subsurface beneath the site (see [7.2\)](#page-14-0). [Table X6.8](#page-55-0) indicates the presence of LNAPL in the subsurface after the excavation of impacted soils near the release area.

X6.5.3.2 Develop the LCSM. The available information was not sufficient to make decisions based on a Tier 1 LCSM. Additional data collection was implemented and a Tier 2 LCSM was developed (see [7.3](#page-14-0) of this guide).

*(1)* Define the top, bottom, and lateral distribution of the LNAPL body (see [6.6.2\)](#page-13-0). [Fig. X6.10](#page-56-0) shows the top, bottom, and lateral dimensions estimated from the site information. The top of the LNAPL body was defined by the soil borings. The top, bottom, and lateral dimension of the LNAPL body were more fully understood after the two ROST/LIF events.

<span id="page-52-0"></span>

<span id="page-53-0"></span>

FIG. X6.6 LNAPL Body Through Time **FIG. X6.6 LNAPL Body Through Time**

<span id="page-54-0"></span>

**FIG. X6.7 LNAPL Body Through Time**

FIG. X6.7 LNAPL Body Through Time

<span id="page-55-0"></span>

**FIG. X6.8 Observed LNAPL Gradient at the Tier 2 Example Site**

**Observed Rate of Lateral LNAPL Movement** 



**FIG. X6.9 Observed Rate of Lateral LNAPL Movement at the Tier 2 Example Site**

**TABLE X6.8 Presence of LNAPL in the Subsurface**

<b>Measures</b>	Yes/No
1. Known LNAPL Release	Yes
2. Observed LNAPL (for example, in wells or other	Yes
discharges)	
3. Visible LNAPL or other direct indicator in samples	Yes
4. Fluorescence response in LNAPL range	Yes
5. Near effective solubility or volatility limits in dissolved	Yes
or vapor phases.	
6. Dissolved plume persistence and center-of mass	Yes
stability	
7. TPH concentrations in soil or ground water indicative	Yes
of LNAPL presence.	
8. Organic vapor analyzer (OVA) and other field	Yes
observations.	
9. Field screening tests positive (for example, paint filter	N/A
test, dye test, shake test)	

*(2)* Define the chemical makeup of the LNAPL (see [6.6.3](#page-13-0) of this guide). While there are no direct LNAPL samples analyzed for chemical content, a number of soil and ground water data sets are available that support this estimation. Soil samples were analyzed using EPA Method 8021B, and benzene is the primary chemical of concern. Ground water samples were analyzed using EPA Method 8021B, and those analytical results are direct indicators of the chemicals of concern in the LNAPL. Analytical results from the most impacted ground water samples can be used to estimate the fraction of chemicals of concern in the LNAPL (see [Appendix X2](#page-25-0) for an example of this calculation). From these results, the mole fraction of the BTEX compounds in the LNAPL are approximately 1.5 %, 3.8 %, 6.2 %, and 13.9 %, respectively.

*(3)* Define the physical properties of the soil and rock materials (see [6.6.4](#page-14-0) of this guide). Laboratory and field testing were completed to characterize the physical properties of the key soil types.

*(a)* Total porosity ranges from 36 to 45 %.

*(b)* LNAPL saturations range from non-detect to 17 % in soil samples with an average of 6.2 % and a median of 2.8 %. Residual LNAPL saturation tests indicated a maximum of 4.7 % for analyses of native samples under three-phase conditions (air-water-LNAPL).

*(c)* Grain size ranges from clay to medium sand. The total fine fraction ranged from 38 to 87 % with median grain size for all samples falling within silt to fine sand ranges.

*(d)* Intrinsic permeability toward water ranged from 0.4 to 103 millidarcy. Intrinsic permeability to kerosene (laboratory LNAPL) ranged from 2662 to 4665 millidarcy for a subset of the same samples, indicating much greater permeability toward LNAPL than water in the same sample cores.

*(e)* The average LNAPL hydraulic conductivity was measured through bail-down tests approximately three years after the release, with results indicating a range from 0.01 to 0.2 ft/day (0.003 to 0.06 m/day). Overall, these results are one to two orders of magnitude smaller than the ground water conductivity; the greatest remaining conductivity is still in the center of the former release area. This is consistent with multiphase theory that suggests LNAPL conductivity will be greatest where LNAPL saturations are highest, all other things being equal. These field LNAPL conductivity results are consistent with the laboratory LNAPL saturation values that were also greatest in the release area. Further, direct observations of LNAPL rates of movement were above 10 ft/day (3 m/day) during the early stages of the release. These field-based LNAPL conductivity results provide a direct indication that the LNAPL body has lost a significant component of mobility since the early stages of the release.

*(f)* The soil capillary " $\alpha$ " values range from  $2.7 \times 10^{-3}$ /cm to  $7.0 \times 10^{-3}$ /cm, indicating a high water retention propensity, consistent with the fine-grained nature of the soils. The capillary N value ranges from 1.9 to 2.5 (see [Appendix X3](#page-30-0) for the capillary equations).

 $(g)$  The LNAPL density is approximately 0.84  $g/cm<sup>3</sup>$ , and the viscosity varies between 1 and 2.5 centipoises (based on laboratory fluid measurements). The water-air interfacial tension is approximately 73 dynes/cm, the oil-water interfacial tension varies from 18 to 25 dynes/cm, and the air-oil interfacial tension is about 26 dynes/cm.

X6.5.3.3 Determine the type-area distribution of LNAPL mass and chemicals of concern (see [7.3.5](#page-14-0) of this guide). Given the information in  $X6.5.3.2$ , the Tier 2 LNAPL-type area is approximately 950 ft (290 m) in length and 750 ft (230 m) in width. The maximum thickness of LNAPL smear zone is 14 ft

<span id="page-56-0"></span>





(4 m), but the statistical average for the plume is approximately 4.5 ft (1.4 m). The ongoing monitoring data combined with the advanced data indicate the LNAPL body footprint is effectively stable as discussed in X6.5.3.4*(1)*, so that the source zone can be evaluated as a static LNAPL body generating dissolved- and vapor-phase plumes. The total remaining volume of the LNAPL body is estimated at approximately 500 000 gal (1 892 700 L).

X6.5.3.4 Define the exposure pathways and risks (see [6.6.5](#page-14-0) and [6.6.6](#page-14-0) of this guide) based on using the property boundary as the point of compliance.

*(1)* The LNAPL body was observed to be mobile during the early stages of the release. Following initial remedial actions, the direct field observations indicate negligible LNAPL body movement. Simple screening calculations using the multiphase form of Darcy's Law as provided in [Appendix X3](#page-30-0) indicate a theoretical mobility potential of less than 3 ft/year (0.9 m/year) at the edges of the LNAPL body. Calculations were performed using field measured LNAPL conductivity, LNAPL gradient, saturation, porosity, capillarity, and other pertinent site parameters. In total, these indicate a low probability of LNAPL movement to the point of compliance.

*(2)* Similarly, the ground water dissolve-phase plume appears stable based on direct field observations coupled with measurements of geochemical indicators of natural attenuation (MNA parameters). The MNA parameters indicate biodegradation of the dissolved-phase compounds is occurring. Given these overall conditions, a range of transport estimates indicated that dissolved phase spreading down gradient from the LNAPL body would not likely exceed a distance of 300 to 450 ft (91 to 137 m) at a benzene RBSL of 5 µg/L.

*(3)* For both LNAPL and ground water, field observations combined with screening modeling information indicate that the ground water and LNAPL can be monitored to verify that RBSLs are met at the point of compliance.

*(4)* The current and future land use is agricultural.

*(5)* A worker receptor was considered for the area above the LNAPL body and the vapor- phase plume. Outdoor air inhalation was identified as the applicable exposure pathway. The concentrations in outdoor air were below the RBSL for worker inhalation. No additional remedial actions are necessary for this exposure pathway.

*(6)* Because the vadose zone soil impacts were removed with the initial remedial action of soil and the depth to the water table is greater than 15 ft, there are no remaining food-chain exposure pathways.

*(7)* Additional cleanup requirements and drivers. There are no risk-based drivers for additional cleanup. The site attributes now driving corrective action decisions are based on the location of the point of compliance (that is, the property line several hundred feet away) and the apparent absence of continued LNAPL body and ground water plume mobility (that is, no further impact to the ground water resource and absence of receptors at the site). The state agency requires the consideration of additional cleanup of LNAPL if it is shown to be practicable and cost-effective; this is a non-risk factor. The LNAPL site objectives are shown in Table X6.9.

*(8)* Four remedial action options were compared to ensure that exposure pathways are managed and to address potential further LNAPL cleanup. LNAPL skimming and hydraulic pumping were considered using a recovery trench and wells in-place. In-situ air sparging was evaluated, as was MNA. The results of these benefit-cost evaluations are shown in [Tables](#page-58-0) [X6.10 and X6.11.](#page-58-0) Review of these site-specific results show that engineered remediation can meet several of the key remediation benefit metrics, with air sparging scoring the best, followed by MNA and hydraulic pumping, with skimming scoring poorest. In comparing cost, safety, and land impacts, MNA scored lowest (lowest cost and lowest impact). In the given decision matrix the option with the highest benefit score and the lowest cost score is the one that is the best option to implement.

*(9)* The decision on this site was to move forward with an MNA program. Several of the important factors were as follows:

*(a)* Excavation and LNAPL recovery remedial action had already been implemented.

*(b)* There were no human health risks under current site conditions.

*(c)* The logistics of installing an engineered system in a remote rural land are difficult.

*(d)* The property owner needed to put the property back into agricultural use.

*(10)* Based on the site information listed in *(9)*, a ground water management zone encompassing the LNAPL body and the dissolved-phase ground water plume was established. A ground water monitoring well network was put in place to confirm the expected LNAPL body and ground water plume immobility and natural degradation. This generalized approach to plume management through monitoring is shown visually in [Fig. X6.11.](#page-60-0)





<span id="page-58-0"></span>

*(11)* The outcomes for this site would likely be different in another regulatory, ground water, or land use situation. The weighing of factors considered is also important, and in this case, the property owner's requirements for the land were very important to the process. Similarly, the extensive options evaluation that was performed for this site and only briefly

#### **TABLE X6.11 Example 2 Remedial Action Decision Matrix—Costs**

NOTE 1—For the example above, IAS/SVE would be the most viable potential remedial action in achieving benefits, but it is also costly. MNA achieves the most desired benefits at the lowest cost and is therefore the optimal option for this specific site. If answers are uncertain, then pilot testing would typically be done to verify key benefit and cost assumptions. Note that for explanatory purposes, it is assumed that none of the remediation metrics are currently met at the site based on the LCSM. If one or more remediation metric were already achieved, then the evaluation would proceed based only on the remaining remediation metrics.



summarized here would have different results in different geologic settings. In other words, each potential remedial action has context only when compared against the site-specific LCSM. A technology that is applicable in one set of circumstances may not be applicable in another.

<span id="page-60-0"></span>

FIG. X6.11 Proposed Solution-Plume Management Zone **FIG. X6.11 Proposed Solution—Plume Management Zone**

#### <span id="page-61-0"></span>**X7. GLOSSARY OF TECHNICAL TERMS FOR CHARACTERIZING IMMISCIBLE FLUIDS IN SOIL AND GEOLOGIC MEDIA**

X7.1 air saturation, n—the amount of air occupying the void space of a porous medium, expressed as a fraction or percentage of porosity.

X7.2 Brooks-Corey capillary parameters, n—empirical factors that determine the shape of the wetting fluid retention curve (for example, water saturation versus capillary head) above a wetting fluid table (for example, water table); the *displacement pressure head* parameter controls the beginning height of the curve at a wetting fluid saturation of 100 percent; the *pore-size distribution index* parameter is a measure of pore-size sorting (high values indicate good sorting and low pore-size variability) and controls the shape of the curve of declining wetting fluid saturation with increasing capillary head, to a minimum residual saturation at a maximum capillary head (for example, *irreducible water saturation*); these three parameters can be used for estimating water saturations in an air-water or oil-water system, and for LNAPL saturations in an air-oil system.

X7.3 *bubbling pressure, n*—the pressure at which air will begin to displace water from a porous medium saturated by water; also called *air entry pressure* or the *threshold pressure* associated with the *critical capillary head* in air-water systems.

X7.4 *capillarity, n*—the interaction of the contacting surfaces between immiscible fluids and solids such as mineral grains, fracture surfaces, and well screens. Capillarity results from the adhesion of fluids to the solid surfaces and from cohesion within the fluids, which causes tension forces that distort the interfaces between the fluids into curved surfaces.

X7.5 *capillary action, n*—movement of fluids in porous media caused by capillary forces such as interfacial tensions between two immiscible fluids and the solid surfaces, for example, the rise of water in capillary tubes.

X7.6 *capillary forces, n*—the sum of adhesion forces between fluids and the solid surfaces and the cohesive forces within and between two or more immiscible fluids.

X7.7 *capillary head, n*—the pressure head of a wetting or non-wetting fluid in a porous medium, equivalent to the capillary pressure divided by the product of the acceleration of gravity and the fluid density.

X7.8 *capillary parameters, n* —empirical parameters that control the shape of a fluid saturation profile curve near a water table; defined for an air-water fluid pair in porous media by the conceptual models of van Genuchten (1980) (Ref **[\(9\)](#page-67-0)**) and Brooks-Corey (1964) (Ref **[\(10\)](#page-67-0)**).

X7.9 *capillary pressure, n*—the difference in non-wetting and wetting fluid pressures across a sharp interface averaged over a representative volume of the porous medium to give a macroscopic relationship to fluid saturations; determined by subtracting the wetting fluid pressure from the non-wetting

fluid pressure. In practice, a negative capillary pressure may be referred to as positive *suction pressure*.

X7.10 *contact angle, n*—the angle between the interface separating two immiscible fluids and a solid surface, measured through the denser fluid. For a given pair of fluids, the contact angle is not a constant but varies with the direction of immiscible displacement, thereby causing the relation between wetting fluid saturation capillary pressure to be *hysteretic*.

X7.11 *critical capillary head, n*—the capillary head at which air begins to displace water from a saturated porous media. In water-drainage tests, it is the capillary head at which the porous medium sample begins to drain, thereby allowing air to enter the sample; synonymous with *displacement pressure head*.

X7.12 *displacement pressure, n*—a parameter in the Brooks-Corey capillary-saturation model that represents the threshold value of capillary pressure at which the wetting fluid begins draining; empirically determined value of the capillary pressure at an effective water saturation value of 1; synonymous with *non-wetting fluid entry pressure* and the *bubbling pressure* in an air-water system.

X7.13 *drainage, n*—an immiscible displacement process driven by gravity forces during which a non-wetting fluid displaces a wetting fluid that initially saturates a porous medium.

X7.14 *effective porosity, n*—the amount of interconnected void space (within intergranular pores, fracture openings, and the like) available for fluid movement; generally less than total porosity.

X7.15 *effective saturation, n* —the ratio of wetting fluid saturation minus its residual saturation to the maximum wetting fluid saturation minus its residual saturation; used to define the *pore-size distribution index* in the Brooks-Corey capillarysaturation model and to simplify the expressions for the van Genuchten capillary-saturation model and the Mualem and Burdine hydraulic conductivity models.

X7.16 *entrapped air, n*—residual air in the form of discontinuous bubbles entrapped in the void space of a porous medium resulting from the imbibition of a wetting fluid (water or LNAPL), as may occur with a rising water table or free LNAPL table.

X7.17 *fluid density, n*—a measure of the fluid mass per unit volume that is temperature dependent; fluid density is usually expressed in gm/cm<sup>3</sup>, with dimensions of mass/volume.

X7.18 *fluid potential, n*—the amount of work performed isothermally and reversibly in moving a unit mass of fluid from a reference state to a point within a flow system, in dimensions of length<sup>2</sup>/time<sup>2</sup>; equivalent to the mechanical energy per unit

mass of fluid, which can be converted to hydraulic head by dividing by the acceleration of gravity.

X7.19 *fluid pressure, n*—the force per unit area acting at a point within a fluid, in dimensions of mass/length  $\times$  time<sup>2</sup>.

X7.20 *fluid pressure head, n* —fluid pressure divided by the product of the acceleration of gravity and fluid density, in dimensions of length; equivalent to the height of a column of the fluid that can be supported by the fluid pressure at a point above a datum.

X7.21 *fluid saturation, n*—the fraction or percentage of void space in a porous medium that is occupied by a particular fluid; used when more than one immiscible fluid is present.

X7.22 *fluid viscosity, n*—a measure of the resistance of a fluid to deform under a shear stress, resulting in a resistance to flow that is temperature dependent; dynamic viscosity is expressed in units of centipoises (cp), with dimensions of mass/length  $\times$  time; pure water at 25 degrees Celsius having a viscosity of 1 cp; the kinematic viscosity is equivalent to dynamic viscosity divided by the fluid specific gravity and is expressed in units of centistokes, with dimensions of length $2/$ time.

X7.23 *free water, n*—soil water that is not held against gravity by capillary forces associated with soil tension but is free to move in response to gravity forces.

X7.24 *hysteresis, n*—the influence of the previous history of drainage and imbibition of a wetting fluid during cyclic immiscible displacement events; caused by changes in the contact angle between the wetting and non-wetting fluids when the wetting fluid is advancing or receding over the solid surfaces of the porous medium, and thereby making capillary pressure-fluid saturation relationships vary with the direction of immiscible displacement.

X7.25 *imbibition, n*—an immiscible displacement process driven by capillary forces during which a wetting fluid displaces a non-wetting fluid that initially saturates a porous medium (or occupies all available void space at saturations above the wetting fluid irreducible saturation).

X7.26 *immiscible displacement, n*—the simultaneous flow of two or more immiscible fluids in a porous medium.

X7.27 *immiscible fluids, n*—two or more fluids that are either insoluble or sparingly soluble in each other, for example, subsurface air, LNAPL, and groundwater; the contacting surface(s) between immiscible fluids are assumed to be sharp curved interfaces in porous media.

X7.28 *immobile LNAPL, n*—LNAPL in a porous medium that exists at or below its residual saturation and is therefore incapable of migrating.

X7.29 *interfacial tension, n* —a form of energy arising from the attraction of molecules in the interior of a fluid phase and those at the surface of contact with another immiscible fluid or solid substance; equivalent to the amount of work that must be done to separate a unit area of one fluid from another fluid or substance, in units of dynes/cm.

X7.30 *irreducible saturation, n*—a residual saturation of a wetting fluid reached at the endpoint of gravity drainage (for example, applies to water in both air-water and oil-water systems).

X7.31 *LNAPL conductivity, n*—the volumetric rate at which mobile LNAPL can flow across a unit area oriented at a right angle to a unit LNAPL potentiometric gradient; equivalent to hydraulic conductivity of the media multiplied by the relative permeability of the LNAPL and the ratio of LNAPL density to viscosity, relative to water density and viscosity, having dimensions of length/time.

X7.32 *LNAPL mobility, n*—the ease with which LNAPL can migrate in a porous medium in response to capillary and gravity forces; related, by various writers, to the LNAPL conductivity, LNAPL effective porosity, or LNAPL potentiometric head gradient at a given location in an LNAPL plume.

X7.33 *LNAPL plume stability, n*—a condition in which a spreading LNAPL plume comes into equilibrium with weathering processes that remove LNAPL mass, with physical processes that transfer the LNAPL to an immobile state within a *smear zone*, and by the non-wetting fluid entry pressure of media at the leading edge of the LNAPL plume halting further lateral migration into media having no LNAPL.

X7.34 *LNAPL potentiometric gradient, n*—the change in LNAPL potentiometric head per unit distance in a given direction; if not specified, the gradient direction is understood to be the direction of the maximum rate of decrease in head with distance; it may or may not be related to the water-table gradient in both direction and magnitude, depending on the degree of heterogeneity and anisotropy of the porous or fractured medium.

X7.35 *LNAPL potentiometric head, n*—the sum of the LNAPL pressure head and the elevation above a standard datum of the point at which pressure head is measured.

X7.36 *LNAPL potentiometric surface, n*—the surface that represents the potentiometric head of the mobile LNAPL within a continuous body of mobile LNAPL, or the *LNAPL plume*; equivalent to the surface along which the LNAPL fluid pressure is equal to atmospheric pressure, which may also be called the *LNAPL table*, or *air-oil table*.

X7.37 *LNAPL pressure head, n* —the height of a column of LNAPL that can be supported by the LNAPL fluid pressure at a point within in a mobile LNAPL layer.

X7.38 *LNAPL saturation, n*—the amount of LNAPL occupying the void space of a porous or fractured medium, or both, expressed as a fraction or percentage of porosity.

X7.39 *LNAPL saturation profile, n*—the vertical distribution of LNAPL saturations through a layer of mobile LNAPL in media near the water table, as controlled by the physical

properties of the solid matrix and the fluids.

X7.40 *LNAPL specific discharge, n*—the product of LNAPL conductivity and LNAPL potentiometric gradient, in dimensions of velocity (length/time).

X7.41 *LNAPL specific yield, n* —the volume of LNAPL that will drain from a unit area of mobile LNAPL divided by a unit decline in LNAPL potentiometric head, expressed as a dimensionless fraction.

X7.42 *LNAPL transmissivity, n* —the volumetric rate at which LNAPL can flow through a unit width of a mobile LNAPL layer at a given location under a unit LNAPL potentiometric gradient, and having dimensions of length $2/$ time; in a homogeneous porous medium, approximately equal to the product of the thickness of the LNAPL layer and the mobile LNAPL conductivity averaged over the layer.

X7.43 *matric potential, n*—the fluid potential in the partially-saturated vadose zone above the water table; being less than the reference state at the water table where the fluid potential is zero, it is always negative and can be converted to an equivalent capillary pressure.

X7.44 *non-wetting fluid, n*—a fluid that, in the presence of an immiscible wetting fluid in a pore space, is preferentially excluded from making direct contact with the solid surfaces, hence may only be in direct contact with a thin film of wetting phase that coats the solid surface; the contact angle made by the solid surface and the interface between the fluids will be >90 degrees.

X7.45 *non-wetting fluid entry pressure, n*—the fluid pressure at which a non-wetting fluid will begin to displace a wetting fluid from a porous medium saturated with the wetting fluid.

X7.46 *non-wetting fluid entry pressure head, n*—the nonwetting fluid head at which it begins to enter a porous medium saturated with a wetting fluid; equivalent to non-wetting fluid entry pressure divided by the specific gravity of the nonwetting fluid.

X7.47 *oil conductivity, n*—synonymous with *LNAPL conductivity*.

X7.48 *pore-size distribution index, n*—a parameter in the Brooks-Corey capillary-saturation model determined by the slope of a line representing the wetting fluid capillary headeffective saturation relationship on a log-log scale; larger values are associated with well-sorted coarse-textured media and smaller values are associated with poorly-sorted finetextured media.

X7.49 *porous medium, n*—an earth material (soil, sediment, rock type, etc.) that contains interconnected pores that allow for the storage and movement of fluids; characterized by physical properties such as grain size, dry density, hydraulic conductivity, capillary parameters, and porosity.

X7.50 *potentiometric gradient, n*—the change in potentiometric head over a distance along a potential flow path; if not specified, the gradient direction is understood to be the direction of the maximum rate of decrease in head with distance; equivalent to *hydraulic gradient*.

X7.51 *potentiometric head, n* —the sum of the groundwater pressure head and the elevation above a standard datum of the point at which that pressure head is measured; equivalent to *hydraulic head*.

X7.52 *potentiometric surface, n*—the surface that represents the potentiometric head of the groundwater over an area and within an aquifer or aquitard; when the groundwater is shallow and unconfined and the fluid pressure is equal to atmospheric pressure, the potentiometric surface is the *water table*.

X7.53 *primary porosity, n*—porosity associated with intergranular void space between mineral grains or other particles (pebbles, fossils, construction debris, etc.) in soil, sediments, or rock formations; may co-exist with secondary and tertiary forms of porosity.

X7.54 *relative permeability, n*—a measure of the relative ability of a porous medium to transmit a particular fluid when other immiscible fluids are present, hence depends on the fluid saturation; expressed as a number between 0 and 1 that can be multiplied by the permeability determined when the given fluid is the *only* fluid present in the medium.

X7.55 *representative elemental volume, n*—the smallest volume of soil or rock that captures the variability of pore and grain sizes, or other structures within the soil or rock, thereby representing a statistically homogeneous sample.

X7.56 *residual fluid saturation, n*—for a given fluid and porous medium, the saturation at which the fluid becomes immobilized by capillary forces and can not be moved by gravity forces.

X7.57 *residual LNAPL saturation, n*—for a given LNAPL and porous medium, the saturation at which the LNAPL becomes immobilized by capillary forces. In the vadose zone, LNAPL residual saturation is the fluid saturation endpoint of gravity drainage of LNAPL, while in the saturated zone, it is the endpoint of imbibition of groundwater into the mobile LNAPL zone, a process that entraps isolated globules of LNAPL in the pores.

X7.58 *residual water saturation, n*—the maximum amount of water in a soil that will *not* contribute to water flow because of blockage from the flow paths or strong adsorption onto the solid phase surfaces.

X7.59 *retention curve, n*—a curve made by plotting the wetting fluid saturation versus capillary pressure or capillary head, and representing the amount of wetting fluid retained in the medium by capillary forces against gravity at equilibrium; referred to as the *soil moisture characteristic curve* in engineering literature.

X7.60 *scanning curves, n*—wetting fluid capillary pressuresaturation pathways within the bounding drainage and imbibition curves; a wetting scanning curve and drying scanning <span id="page-64-0"></span>curve pair can form a *hysteresis loop* within the bounding curves.

X7.61 *secondary porosity, n*—porosity associated with joints, fractures, faults, and bedding planes in rock formations and have not been significantly enlarged by dissolution (see Guide D5717).

X7.62 *soil tension, n*—a term used for capillary pressure in partially-saturated soils, which can hold water (or another wetting fluid) in the capillary fringe above the water table (or another fluid table); causes the rise of water in capillary tubes and is usually expressed as the height of water rise above the water table, the reference datum; synonymous with the term *soil suction*.

X7.63 *surface tension, n*—the interfacial tension between a liquid and its own vapor phase, in units of dynes/cm.

X7.64 *tensiometer, n*—a device for measuring the capillary head of water at a specified depth in the vadose zone above the water table. By adding the elevation of the base of the tensiometer to the capillary head, the user obtains potentiometric head of the water in the partially-saturated vadose zone.

X7.65 *tertiary porosity, n*—porosity associated with natural macropores in soil or dissolution- enlarged openings in carbonate rocks developed after and often in relation to secondary porosity (see Guide [D5717\)](#page-2-0).

X7.66 *van Genuchten capillary parameters, n*—empirical factors that determine the shape of the wetting fluid retention curve (for example, water saturation versus capillary head) above a wetting fluid table (for example, water table); the *van* *Genuchten* α parameter controls the curve for capillary head values ranging from zero to approximately the medium's displacement pressure and the *van Genuchten n* parameter controls the shape of the curve for capillary head values above the displacement pressure, to a residual saturation at maximum capillary head (for example, *irreducible water saturation*); these three parameters can be used estimating for water saturations in an air-water or oil-water system, and for LNAPL saturations in an air-oil system.

X7.67 *water content, n*—the volume of water per bulk volume of representative elemental volume (volumetric basis); may be expressed as the volume of water per unit dry weight of solids within the representative elemental volume (dry weight basis).

X7.68 *water saturation, n*—the amount of water occupying the void space of a porous medium, expressed as a fraction or percentage of porosity.

X7.69 *wettability, n*—the tendency of a solid material (for example, mineral grains, fracture surfaces, well screen) to prefer to be in direct contact with a *wetting* fluid over a *non-wetting* fluid that shares the same void space. In most earth materials, water is the wetting fluid, air is the non-wetting fluid, and LNAPL behaves as a wetting fluid relative to air and a non-wetting fluid relative to water.

X7.70 *wetting fluid, n*—a fluid that, in the presence of an immiscible non-wetting fluid in a pore space, will preferentially spread over the solid surface, thereby displacing the non-wetting fluid; the contact angle made by the solid surface and the interface between the fluids will be <90 degrees.

#### **X8. GLOSSARY OF TECHNICAL TERMS FOR CHARACTERIZING THE NATURE AND MIGRATION OF CHEMICALS DE-RIVED FROM LNAPL IN SOIL AND GEOLOGIC MEDIA**

X8.1 *adsorbed phase, n*—part of a multiphase system that includes the contaminant mass adhering to the surfaces of minerals that are contacting the vapor or liquid phase(s) in which the contaminant is dissolved.

X8.2 *adsorption, n*—the process of adhesion of molecules derived from vapor or liquid phases to the surface of a solid material in contact with the vapor or liquid.

X8.3 *advection, n*—the process by which solutes are transported within a fluid that is moving through porous media, applied to subsurface air or water.

X8.4 *aerobic, adj*—a condition in which atmospheric or dissolved oxygen is present in an environment; commonly used to describe a biological process that occurs in the presence of oxygen.

X8.5 *anaerobic, adj*—a condition in which atmospheric or dissolved oxygen is *not* present in an environment; commonly used to describe a biological process that occurs in the absence of oxygen.

X8.6 *aqueous phase, n*—the water portion of a multiphase system consisting of two or more fluids (for example, air, LNAPL, water), a solid mineral phase, and possibly an adsorbed phase; the aqueous phase may include dissolved chemicals derived from the LNAPL and the other phases.

X8.7 *aquifer, n*—a geologic formation, or strata within a formation, that has the sufficient water-storage capacity and transmissivity (permeability and thickness) to provide economically usable quantities of groundwater to wells.

X8.8 *aquifer transmissivity, n*—the volume of groundwater that will flow per unit time across a vertical section of unit width through the full thickness of an aquifer oriented at a right angle to a unit hydraulic gradient, with dimensions of length $^{2}$ / time; equivalent to the product of saturated thickness and average horizontal hydraulic conductivity of the aquifer.

X8.9 *aquitard, n*—a geologic formation, or strata within a formation, that has insufficient permeability and thickness to provide economically usable quantities of groundwater to wells; when aquitards overlie and underlie a confined aquifer,



they restrict the flow of groundwater to and from the aquifer.

X8.10 *biodegradation, n*—the decomposition of organic material by microorganisms, involving processes which transform or alter the structure of chemicals through enzymatic and metabolic action.

X8.11 *bulk density, n*—the dry density of an earth material (soil, sediment, saprolite and the like); equivalent to the mass of a material divided by its volume, including the negligible mass of air.

X8.12 *chemical mass flux, n*—the flow of mass per unit time across a discrete cross-sectional area within a fluid in a porous medium. Mass flux begins with the transfer of chemicals from the LNAPL to subsurface air and water and continues with the movement of chemical mass dissolved within the vapor and aqueous phases; it may involve partitioning of chemicals from groundwater back to the vadose zone or to indoor air.

X8.13 *chemical mass losses, n* —the mass transferred from one phase to another by partitioning over a given time period (for example, from LNAPL to groundwater, vapor, and adsorbed phases), where the loss of mass is accompanied by a decline in chemical concentration in the source phase, but the chemical concentration in the receiving phase may remain nearly constant at the point of contact. The rate of mass loss is driven by the concentration gradients across phase boundaries, background concentrations and flow rates of the receiving phase, and rates of chemical adsorption and degradation in the receiving phase environment.

X8.14 *Darcy velocity, n*—the volumetric discharge per unit area of fluid flow through a porous material; equivalent to the terms *Darcy flux* and *specific discharge* with dimensions of length/time.

X8.15 *dispersion, n*—the spreading and blending of a chemical contaminant within a flowing fluid (usually air, surface water, or groundwater) caused by molecular diffusion and mechanical mixing related to spatial variations in flow velocity and direction.

X8.16 *dispersion coeffıcient, n*—the sum of the coefficients of mechanical dispersion and molecular diffusion; related to the direction of the fluid flow and used in chemical mass transport calculations.

X8.17 *dispersivity, n*—a property of a porous medium and specified fluid that determines the dispersion characteristics of any contaminant by relating flow velocity to the directional dispersion coefficient.

X8.18 *effective fluid conductivity, n*—a fluid-specific hydraulic conductivity with dimensions of length/time that accounts for the density and viscosity of the fluid, and for the relative permeability of the fluid when one or more fluids coexist in the same void space; because it is a function of fluid saturation, effective fluid conductivity varies with position within a continuous LNAPL layer, and commonly applied to the aqueous or LNAPL phase.

X8.19 *effective fluid transmissivity, n*—a fluid-specific transmissivity with dimensions of length<sup>2</sup>/time that integrates the values of effective fluid conductivity along a vertical profile through a layer of mobile LNAPL, and commonly applied to the aqueous or LNAPL phase.

X8.20 *effective porosity, n*—the amount of interconnected void space (within intergranular pores, fracture openings, and the like) available for fluid movement; generally less than total porosity.

X8.21 *effective solubility, n* —the maximum dissolvedphase concentration in vapor and aqueous fluids (for example, subsurface air or water) of a chemical derived from, and in chemical equilibrium with, an LNAPL source; determined by the pure-phase solubility and molar concentration of the chemical in the LNAPL and by the temperature and chemical quality of the contacting fluids.

X8.22 *fluid density, n*—the mass of fluid per unit volume, depending on the ambient temperature and pressure.

X8.23 *fraction of organic carbon, n*—fraction by weight of natural organic matter in the soil that, along with the organic portioning coefficient (Koc), controls chemical partitioning from the aqueous to the adsorbed phase.

X8.24 *Freundlich isotherm, n* —an empirical mathematical relationship between the mass of solute adsorbed onto a unit mass of soil for a given solute concentration and temperature.

X8.25 *grain density, n*—the density of soil grains, equivalent to the mass of the granular material per unit volume. For many types of sediment, the grain density is close to 2.65 g/cc reflecting a silica-rich composition.

X8.26 *groundwater, n*—water in the saturated zone below a perched or regional water table.

X8.27 *groundwater flow net, n* —a two-dimensional (or three-dimensional) graphical depiction of a set of groundwater flow lines (or surfaces) intersecting with potentiometric contour lines (or surfaces) that illustrates the pattern of steady groundwater flow through part of a larger *flow system* defined by a recharge area, discharge area, and boundaries, which are controlled by climatic setting, topographic features, the hydraulic properties of geologic formations, and distribution of man-made stresses (for example, pumping or injection wells).

X8.28 *groundwater mass flux, n*—the mass of dissolved contaminant moving with groundwater per unit time across a unit area in a porous medium in response to the prevailing hydraulic gradient and effective fluid conductivity for water; equivalent to the product of groundwater volumetric discharge and contaminant concentration, having dimensions of mass/ time.

X8.29 *hydraulic conductivity, n*—the volume of water that will flow per unit time across a unit square area oriented at a right angle to a unit hydraulic gradient, with dimensions of length/time.

X8.30 *linear pore velocity, n* —the averaged linear rate of movement of a given fluid through the pore space in which the fluid phase is continuous, equivalent to the Darcy velocity of the fluid divided by effective porosity, and having dimensions of length/time.

X8.31 *longitudinal dispersion, n*—mechanical mixing and molecular diffusion of a contaminant in a fluid measured in the direction of fluid flow.

X8.32 *mass content, n*—the mass of any liquid phase divided by the mass of soil in which it is present, for example, *water content*, used in geotechnical measurements, is a type of mass content.

X8.33 *molar concentration, n* —a chemical concentration expressed as the number of moles of the chemical solute in a 1-L solution with a solvent; for example, the moles of a dissolved contaminant per liter of groundwater, or per liter of air at standard temperature and pressure.

X8.34 *mole, n*—a basic unit of chemical mass associated with Avogadro's number of atoms or molecules of an element or compound, equivalent to the atomic weight of the element, or molecular weight of the compound, in grams.

X8.35 *mole fraction, n*—a dimensionless ratio of the number of moles of a solute compound divided by the total number of moles of all compounds in the solution, where the solute is a contaminant and the solution is either a nonaqueous, aqueous, or vapor phase.

X8.36 *Monte Carlo simulation, n*—a procedure for estimating the range and frequency of occurrence of values of model output (for example, the concentration of a contaminant at a hypothetical exposure point) that accounts for probabilistic input variables, each of which have a range and frequency of occurrence within the model domain.

X8.37 *organic carbon partitioning coeffıcient (Koc), n*—the portioning coefficient for the adsorption of an organic solute onto organic carbon within a porous medium; a measure of the propensity for an organic chemical to partition preferentially into the organic phase; often expressed as the log  $K_{\text{oc}}$ , where larger values indicate low mobility of the solute within the subsurface.

X8.38 *partitioning, n*—the process of transferring chemical mass from one phase another adjoining phase; at chemical equilibrium, the chemical potentials of the transferring chemical in the two phases become equal.

X8.39 *partitioning coeffıcient, n*—the ratio of mole fractions, or of molar concentrations, for a chemical solute in two adjoining phases at chemical equilibrium; when associated with the transfer of a solute to the adsorbed phase, it is called the *distribution coefficient*  $(K_d)$ , and is expressed as the mass of adsorbed solute per mass of solid phase divided by the solute concentration in the solution (for example, groundwater); in laboratory measurements, the distribution coefficient is equivalent to the slope of a linear Freundlich isotherm.

X8.40 *perched water table, n* —a water table associated with a local lens of saturated porous media, caused by localized recharge and/or a relatively thin and less permeable stratum called a *perching horizon*.

X8.41 *phase, n*—a distinct state of matter within a chemical system, identical in chemical composition but separated from other phases by a boundary across which chemical mass transfer may take place; liquid, solid, gaseous, adsorbed, or colloidal phases of the same chemical substance may coexist in chemical equilibrium within a chemical system.

X8.42 *saturated zone, n*—generally understood to be that part of the subsurface in which the void space is fully saturated by *groundwater*.

X8.43 *solubility, n*—the maximum equilibrium concentration of a chemical solute in a solvent at a given temperature and pressure; the solvent can be any fluid, that is, air, water, or LNAPL; the standard reference solubility for an organic compound in water assumes that only water and the pure compound are present in the solution (see definition of *effective solubility*).

X8.44 *transverse dispersion, n*—mechanical mixing and molecular diffusion of a contaminant in a migrating fluid measured at a right angle to the direction of fluid flow, where the horizontal or vertical direction of dispersion must be specified.

X8.45 *vapor diffusion effıciency, n*—a dimensionless factor from 0 to 1 that is multiplied by the vapor mass flux, which reduces the calculated flux exiting the LNAPL source zone. It accounts for geologic and man-made impedances to free volatilization from the formation LNAPL/air interface, or to natural attenuation processes and vapor diffusion through the vadose zone to the atmosphere.

X8.46 *vapor mass flux, n*—the mass of contaminant in a vapor phase, from an LNAPL or groundwater source, that moves per unit time through a unit area of the vadose zone. The flux may vary as a function of position in the vadose zone due to spatial variations in water content and air permeability of soil strata, and is influenced by natural attenuation processes including adsorption, dispersion, and biodegradation.

X8.47 *water table, n*—an undulating surface through porous media along which the water pressure is equal to local atmospheric pressure; identified by the static water level in wells that penetrate a short distance into a water-saturated zone; a local shallow water table may be perched above a deeper regional water table with an unsaturated zone in between the two saturated zones.

<span id="page-67-0"></span>X8.48 *water table gradient, n* —the change in water table elevation over a horizontal distance, assumed to be in the direction of maximum elevation change unless stated otherwise, and may be expressed either as a dimensionless fraction or in length/length (for example, ft/mile); equivalent to the *hydraulic gradient* measured in the horizontal direction, which serves as the primary driving force for the movement of shallow groundwater below the water table.

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