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Standard Guide for NAPL Mobility and Migration in Sediments – Evaluation Metrics[1]

This standard is issued under the fixed designation E3282; 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 (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This guide discusses methodologies that can be applied to evaluate the potential for the movement (that is, pore-scale mobility or NAPL body-scale migration) of non-aqueous phase liquid (NAPL) in sediments. NAPL movement assessment in sediments is significantly different than in upland soils. As such, the frameworks for evaluating NAPL movement in upland soils have limited applicability for sediments. In particular, because upland NAPL conceptual site models may not be applicable to many sediment sites, this guide provides a framework to evaluate whether NAPL is mobile (at the pore scale) or migrating (at the NAPL body scale) in sediments.

1.2 Assessment of the potential for NAPL to move in sediment is important for several reasons, including (but not limited to) evaluation of risk to potential receptors, the need for potential remedial action, and potential remedial strategies. For example, if the NAPL is migrating, sensitive receptors may be impacted and this will influence the choice and timing of any remedy selected for an area of the sediment site. If the NAPL is not mobile or migrating, then remedial actions may not be warranted.

1.3 This guide is applicable at sediment sites where NAPL has been identified in the sediment by various screening methods and the need for a NAPL movement evaluation is warranted (Guide E3248).

1.4 Petroleum hydrocarbon, coal tar, and other tar NAPLs (including fuels, oils, and creosote) are the primary focus of this guide. These forms of contamination are commonly related to historical operations at refineries, petroleum distribution terminals, manufactured gas plants (MGPs), and various large industrial sites.

1.5 Although certain technical aspects of this guide apply to other NAPLs (for example, dense NAPLs [DNAPLs] such as chlorinated hydrocarbon solvents), this guide does not completely address the additional complexities of those DNAPLs.

1.6 The goal of this guide is to provide a sound technical basis to determine if NAPL at the site is mobile or immobile at the pore scale, and if mobile, whether it is stable or migrating at the NAPL body scale. The potential for NAPL movement in the sediment is a key component in the development of the conceptual site model (CSM) and in deciding what remedial options should potentially be chosen for the site to reduce potential risks to human health and ecological receptors.

1.7 This guide can be used to help develop, or refine, a CSM for the sediment site. A robust CSM is typically needed to optimize potential future work efforts at the site, which may include various risk management and remedial strategies for the site, as well as subsequent monitoring after any remedy implementation.

1.8 This guide considers the mobility of NAPL in sediments that originated from three broad categories of potential NAPL emplacement mechanisms (Guide E3248).

1.8.1 Migration of NAPL by advection (flow through the soil pore network) from an upland site into the pore network of sediments beneath an adjacent water body is one category of NAPL emplacement mechanism. This most commonly occurs within coarse-grained strata in the sediment.

1.8.2 Direct discharge of light NAPL (LNAPL) into a waterway, where it is broken down by mechanical energy to form LNAPL beads, is another category of NAPL emplacement mechanism. Oil-particle aggregates (OPAs) are formed when suspended particulates in surface water adhere to LNAPL beads. Once enough particulates have adhered to an LNAPL bead and the OPA becomes dense enough, it settles through the water column onto a competent sediment surface, where it forms an in situ deposited NAPL (IDN) and may be buried by future sedimentation.

1.8.3 The third category of NAPL emplacement mechanism is DNAPL flow (that is, direct discharge of DNAPL into a waterway), followed by settling through the water column and deposition directly onto a competent sediment surface, where it may be buried by future sedimentation.

1.9 Ebullition-facilitated transport of NAPL from the sediment to the water column by gas bubbles *is not* within the scope of this guide. The evaluation of ebullition and associated NAPL/contaminant transport is covered in Guide E3300.

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Transport of NAPL due to erosional forces (for example, propeller wash) *is not* within the scope of this guide.

1.10 This guide (see Section 5) presents an overall framework to evaluate if NAPL at the site is mobile or immobile at the pore scale, and migrating or stable at the NAPL body scale. It provides guidance on approaches and methodologies that address questions regarding NAPL movement evaluation.

1.11 This guide (see Section 6) discusses the use of data from various laboratory tests (Appendix X1), calculation methodologies, and other methodologies to technically evaluate if NAPL in sediment at various locations in the site is mobile or immobile at the pore scale, and stable or migrating at the NAPL body scale. This evaluation can be performed using tiered and weight of evidence (WOE) frameworks. For example, it may be possible that NAPL is mobile or migrating in one part of the site, but is immobile in other parts of the site. There are currently no industry standard tiered and WOE frameworks to evaluate if NAPL in sediment is mobile or migrating, but illustrative examples of such frameworks are presented in Appendix X2. Case studies demonstrating the application of the example tiered and WOE frameworks exhibited in Appendix X2 are presented in Appendix X3.

1.12 This guide (see Section 7) discusses applicable laboratory centrifuge testing methodologies that are used to evaluate NAPL mobility or immobility at the pore scale under the applicable test conditions (also see Appendix X4). Appendix X5 discusses the laboratory preparation of sediment samples used in centrifuge testing.

1.13 This guide (see Section 8) discusses applicable laboratory water drive testing methodologies that are used to evaluate NAPL mobility or immobility at the pore scale under the applicable test conditions. This section discusses both rigid wall and flexible wall permeameter testing (also see Appendix X6). Appendix X5 discusses the laboratory preparation of sediment samples used in water drive testing.

1.14 This guide (see Section 9) discusses calculation methodologies that provide insight into pore-scale NAPL mobility and NAPL body-scale migration at the site. To perform some of these calculations, NAPL property data such as density, viscosity, and NAPL–water interfacial tension are needed (see Appendix X1). The calculation methodologies include NAPL density versus hydraulic gradient calculations; pore entry pressure calculations; critical NAPL layer thickness calculations; and NAPL pore velocity calculations (also see Appendix X7 and Appendix X8).

1.15 This guide (see Section 10) presents other field observation approaches that are useful in evaluating pore-scale NAPL mobility and NAPL body-scale migration. These methodologies include vertical profiles of NAPL saturation (including isopach mapping of the thickness of unimpacted sediment above the NAPL zone); and installation of monitoring wells in sediment.

1.16 *Units*—The values stated in SI or CGS units are to be regarded as the standard. No other units of measurement are included in this standard.

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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.18 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D425 Test Method for Centrifuge Moisture Equivalent of Soils

D445 Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and Calculation of Dynamic Viscosity)

D854 Test Methods for Specific Gravity of Soil Solids by Water Pycnometer

D971 Test Method for Interfacial Tension of Insulating Liquids Against Water by the Ring Method

D1481 Test Method for Density and Relative Density (Specific Gravity) of Viscous Materials by Lipkin Bicapillary Pycnometer

D2216 Test Methods for Laboratory Determination of Water (Moisture) Content of Soil and Rock by Mass

D5084 Test Methods for Measurement of Hydraulic Conductivity of Saturated Porous Materials Using a Flexible Wall Permeameter

D5856 Test Method for Measurement of Hydraulic Conductivity of Porous Material Using a Rigid-Wall, Compaction-Mold Permeameter

D6836 Test Methods for Determination of the Soil Water Characteristic Curve for Desorption Using Hanging Column, Pressure Extractor, Chilled Mirror Hygrometer, or Centrifuge

D6913 Test Methods for Particle-Size Distribution (Gradation) of Soils Using Sieve Analysis

D7263 Test Methods for Laboratory Determination of Density and Unit Weight of Soil Specimens

D7928 Test Method for Particle-Size Distribution (Gradation) of Fine-Grained Soils Using the Sedimentation (Hydrometer) Analysis

E2531 Guide for Development of Conceptual Site Models and Remediation Strategies for Light Nonaqueous-Phase Liquids Released to the Subsurface

E2856 Guide for Estimation of LNAPL Transmissivity

E3164 Guide for Sediment Corrective Action – Monitoring

E3248 Guide for NAPL Mobility and Migration in Sediment – Conceptual Models for Emplacement and Advection

E3281 Guide for NAPL Mobility and Migration in Sediments – Screening Process to Categorize Samples for

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[2] 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.

Laboratory NAPL Mobility Testing

E3300 Guide for NAPL Mobility and Migration in Sediment – Evaluating Ebullition and Associated NAPL/Contaminant Transport

3. Terminology

3.1 *Definitions:*

3.1.1 *immobile NAPL, n*—NAPL that does not move by advection within the connected void spaces within sediment under specified physical and chemical conditions, as may be demonstrated by laboratory testing, or may be interpreted based on mathematical calculations or modeling. **E3248**

3.1.2 *in situ deposited NAPL (IDN) sediment, n*—NAPL-containing sediment resulting from the deposition of OPAs. **E3248**

3.1.3 *migrating NAPL, n*—NAPL that can move at the NAPL body scale, such that the NAPL body may advectively expand in at least one direction under observed or reasonably anticipated field conditions. **E3248**

3.1.4 *mobile NAPL, n*—NAPL that may move by advection within the connected void spaces of the sediment under specific physical and chemical conditions, as may be demonstrated by laboratory testing, or as may be interpreted based on mathematical calculations or modeling. **E3248**

3.1.5 *non-aqueous phase liquid, NAPL, n*—chemicals that are insoluble or only slightly soluble in water that exist as a separate liquid phase in environmental media. **E3248**

3.1.5.1 *Discussion*—NAPL may be less dense than water (light non-aqueous phase liquid [LNAPL]) or more dense than water (dense non-aqueous phase liquid [DNAPL]).

3.1.6 *NAPL advection, n*—the process of NAPL movement in the subsurface due to pressure and gravitational forces. **E3248**

3.1.7 *NAPL body, n*—sediment where the NAPL present exhibits movement. **E3248**

3.1.7.1 *Discussion*—NAPL is mobile at the pore scale and either stable or migrating at the NAPL body scale. The NAPL body excludes any portion of the NAPL zone where the NAPL is immobile at the pore scale.

3.1.8 *NAPL movement, n*—any process where NAPL exhibits advective flow at any scale within the sediment; NAPL movement includes NAPL mobility at the pore scale and NAPL migration at the NAPL body scale. **E3248**

3.1.9 *NAPL zone, n*—sediment where NAPL is present in any state; the NAPL can be mobile or immobile at the pore scale, and if mobile at the pore scale, stable or migrating at the NAPL body scale. **E3248**

3.1.10 *pore scale, n*—the scale of the connected void spaces within the sediment. **E3248**

3.1.11 *sediment, n*—a matrix of pore water and particles including gravel, sand, silt, clay, and other natural and anthropogenic substances that have settled at the bottom of a tidal or non-tidal body of water. **E3164**

3.1.12 *stable NAPL, n*—NAPL that does not move at the NAPL body scale, such that the NAPL body will not advectively expand in any direction under observed or reasonably anticipated field conditions. **E3248**

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *conceptual site model (CSM), n*—a professional interpretation of site data that serves as a systematic planning instrument, a communication device, and an optimization and decision tool.

3.2.2 *density-driven gradient, n*—hydraulic gradient due to the density or buoyancy of NAPL compared to the surrounding water.

3.2.2.1 *Discussion*—Density-driven gradient is given by the density difference between the NAPL density (ρ_n) and water density (ρ_w) divided by the water density; ρ_n may differ significantly from that of the original NAPL when it was released to the environment, due to NAPL weathering. Site-specific influences on water density (for example, due to salinity) should also be considered.

3.2.3 *dynamic and kinematic viscosities of NAPL (μ_n and v_n), n*—measurements of the internal friction that occurs within NAPL during movement, or of the resistance of the NAPL to flow.

3.2.3.1 *Discussion*—For advectively emplaced NAPLs, viscosities are inversely proportional to the NAPL flow velocity (if migrating); these parameters also may differ significantly from those of the original NAPL due to weathering.

3.2.4 *hydraulic gradient, n*—hydraulic head difference between two points, divided by distance between the points; it is the driving force for water flow and can be a significant factor in NAPL flow.

3.2.5 *immobile saturation, n*—the maximum NAPL saturation where NAPL is still immobile.

3.2.5.1 *Discussion*—In practice, the immobile saturation is the greatest NAPL saturation that does not exhibit pore-scale mobility for a set of specific site conditions (for example, NAPL viscosity, NAPL composition, sediment composition, sediment pore size distribution, NAPL pressure gradient). The immobile saturation can vary, depending on the variability of the site conditions.

3.2.6 *interfacial tension, n*—interfacial tension describes the amount of work that would be required to increase the surface area of an interface between two fluid phases.

3.2.6.1 *Discussion*—Interfacial tension reflects the concept that the interface between two fluids will tend toward a minimum possible surface area (as a drop of oil submerged in water would, in the absence of other forces, take a spherical form). Interfacial tension pairs (generally symbolized as σ, accompanied by a two-letter description of a fluid pair—such as σ_{nw} for NAPL–water interfacial tension) are used in pore entry pressure calculations.

3.2.7 *NAPL footprint, n*—a two-dimensional projection of the NAPL zone in the horizontal plane.

3.2.8 *NAPL saturation (S_n), n*—percentage of the pore space that is occupied by NAPL.

3.2.9 *oil-particle aggregate (OPA), n*—a particle formed in a surface water body resulting from the adherence to (or penetration into) an oil droplet by minerals or organic material.

3.2.10 *relative permeability, n*—for advectively emplaced NAPL, the ratio of the permeability of a fluid at partial saturation to the permeability of the same fluid at 100 % saturation.

3.2.10.1 *Discussion*—In a system containing advectively emplaced NAPL and water, only a fraction of the pore space is occupied by each fluid, so this diminishes the permeability of each fluid. The permeability of a fluid increases with increasing saturation (that is, by increasing the fraction of large pores occupied). At (or below) a threshold NAPL saturation, the relative permeability is zero and the NAPL is immobile (**1**).[3] Relative permeability is not a relevant concept for IDN sediments.

3.2.11 *undisturbed sample, n*—sediment particles that have not been rearranged relative to one another by anthropogenic activity including the collection, transport, and analysis of the sample.

3.2.11.1 *Discussion*—In common usage, the term "undisturbed sample" describes particles that have been rearranged, but only to a slight degree.

3.2.12 *water saturation (S_w), n*—percentage of the pore space of a sediment that is occupied by water.

4. Significance and Use

4.1 Hydrophobic organic liquids (for example, petroleum hydrocarbons, coal tars) may exist in the environment for long periods of time as NAPLs. Standardized guidance and test methods do not exist to assess NAPL movement (both pore-scale mobility and NAPL body-scale migration) in sediment. Literature searches have resulted in a limited body of available and applicable research. Current research has focused on site-specific sediment NAPL movement evaluation approaches.

4.2 Standardized guidance and test methods currently exist for assessing NAPL mobility and migration at upland sites, from organizations such as ASTM International (Guides E2531 and E2856), Interstate Technology and Regulatory Council (**2**), and the American Petroleum Institute (**3, 4**). Approaches commonly used in upland sites may or may not be applicable for any given sediment site. This guide provides perspectives on the applicability of various methodologies for specific sediment conditions.

4.3 This guide describes various methodologies that are useful in sediment NAPL movement evaluation, such as laboratory test methods, calculation approaches, and field observation interpretation. The guide then provides frameworks to evaluate the data generated from these methodologies to determine if the NAPL observed in the sediments under in situ conditions exhibits movement of any kind.

4.4 Important exposure pathways in upland sites are usually not applicable to sediment sites. The U.S. Environmental Protection Agency notes, "Contaminants in the biologically active layer of the surface sediment at a site often drive exposure" (**5**). In aquatic environments, benthic organisms live in the surface sediment to maintain access to oxygenated overlying water. These benthic organisms are at the base of the food chain. If NAPL in subsurface sediment is not migrating, the NAPL will not move into the surface sediment and result in exposure to benthic organisms. NAPL that is stable and only present in subsurface sediment likely does not pose a risk to human or ecological receptors, because there is no completed pathway to exposure if the overlying sediment remains in place (that is, it is not dredged or eroded). With no completed exposure pathway, removal of the NAPL in the subsurface sediment may not be needed during any remedy. Therefore, understanding the potential for movement of NAPL in sediments is a key factor in the management of contaminated sediment sites. Knowledge of NAPL movement is required for developing effective remedial options for NAPL impacted sediments and for long-term management of sediment sites.

4.5 The user of this guide should review the overall structure and components of this guide before proceeding with use, including:

Section 1	Scope
Section 2	Referenced Documents
Section 3	Terminology
Section 4	Significance and Use
Section 5	NAPL Mobility and Migration Evaluation Framework
Section 6	Tiered and Weight of Evidence NAPL Movement Evaluation Approaches
Section 7	Centrifuge Test Methods
Section 8	Water Drive Test Methods
Section 9	Calculation Methods for Potential Vertical Movement of NAPL
Section 10	Field Observation Methodologies
Section 11	Keywords
Appendix X1	Laboratory Analysis Methods Commonly Used in NAPL Movement Evaluations (non-mandatory)
Appendix X2	Illustrative Examples of Tiered and WOE Approaches to Evaluate NAPL Movement (non-mandatory)
Appendix X3	Case Studies (non-mandatory)
Appendix X4	Additional Information on Centrifuge Testing Technology in NAPL Mobility Testing (non-mandatory)
Appendix X5	Laboratory Handling and Preparation of Sediment Cores (non-mandatory)
Appendix X6	Additional Information on Water Drive Test Methods in NAPL Mobility Testing (non-mandatory)
Appendix X7	NAPL Net Vertical Gradient Calculation Method (non-mandatory)
Appendix X8	NAPL Effective Hydraulic Conductivity Estimation Methods (non-mandatory)
References	

4.6 Activities described in this guide should be conducted by persons familiar with NAPL-impacted sediment site characterization techniques and sediment remediation science and technology, as well as sediment NAPL mobility and migration assessment protocols and methodologies.

4.7 This guide may be used by various parties involved in sediment programs, including regulatory agencies, project sponsors, environmental consultants, toxicologists, risk assessors, site remediation professionals, environmental contractors, analytical testing laboratories, data validators, data reviewers and users, and other stakeholders, which may include, but are not limited to, owners, buyers, developers, lenders, insurers, government agencies, and community members and groups.

4.8 This guide is not intended to replace or supersede federal, state, local, or international regulatory requirements. Instead, this guide may be used to complement and support such requirements. Any remedial actions taken should meet the

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[3] The boldface numbers in parentheses refer to the list of references at the end of the standard.

regulatory standards for the regulatory entity under which the corrective action is being performed.

4.9 This guide provides a framework based on overarching features and elements that should be customized by the user, based on site-specific conditions, regulatory context, and program objectives for a particular sediment site. This guide should not be used alone as a prescriptive checklist.

4.10 Assessment of NAPL movement in sediments is an evolving science. This guide provides a systematic, yet flexible, framework to accommodate variations in approaches by regulatory agencies and users, based on project objectives, site complexity, unique site features, programmatic and regulatory requirements, newly developed guidance, newly published scientific research, use of alternative scientifically based methods and procedures, changes in regulatory criteria, advances in scientific knowledge and technical capability, multiple line of evidence (LOE) approaches, and unforeseen circumstances.

4.11 Use of this guide supports multiple LOE approaches, using tiered or WOE evaluation frameworks, for the evaluation of NAPL movement in sediments.

4.12 Use of this guide is consistent with the sediment risk-based corrective action (RBCA) process that guides the user to obtain the appropriate data; acquire and evaluate additional data; and refine goals, objectives, receptors, exposure pathways, and the CSM. As the sediment RBCA process proceeds, data and conclusions reached at each step of the process help focus subsequent evaluation. This integrative process results in efficient, cost-effective decision-making and timely, appropriate response actions for NAPL-impacted sediments.

5. NAPL Mobility and Migration Evaluation Framework

5.1 After NAPL has been confirmed to be present in sediment at a site, the decision should be made whether to perform a NAPL emplacement and movement evaluation for sediment; this can be done using the process described in Fig. 2 of Guide E3248. A full discussion of various emplacement mechanisms is provided in Appendix X1 of Guide E3248. In particular, Fig. X1.9 of Guide E3248 provides guidance on how to interpret the most likely NAPL emplacement mechanism, based on field data. Table 1 briefly contrasts some key differences in characteristics between the three major categories of NAPL emplacement. It is useful (if possible) to understand the NAPL emplacement mechanisms at a site before starting the NAPL movement evaluation. Professional judgment will need to be applied by technical experts to ascertain which evaluation methodologies will be useful at a specific site. The approaches cited may not be applicable at all sediment sites. Appendix X3 of Guide E3248 provides further description of the movement of NAPL at the pore and NAPL body scales.

5.2 As discussed in Section 7.2 of Guide E3248, the NAPL movement evaluation considers the potential for NAPL movement at both the pore (that is, void) and NAPL body scales (Fig. 1). If the evaluation determines that the NAPL is immobile at the pore scale, then it must also be stable at the NAPL body scale, so no further evaluation is necessary. If the evaluation determines that the NAPL is mobile at the pore scale, then further evaluation is required to interpret if the NAPL is stable or migrating at the NAPL body scale.

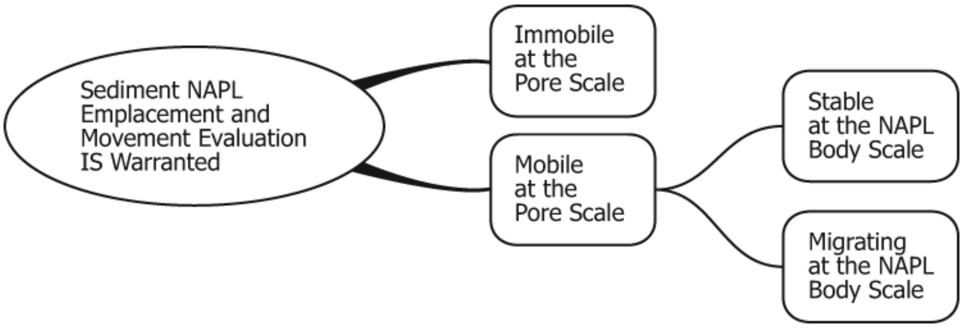
5.3 Fig. 2 presents an example investigative process to evaluate if NAPL at a site is mobile or immobile at the pore scale, as well as if it is migrating or stable at the NAPL body scale. Note that the threshold between mobility and immobility will depend on a number of factors, including sediment texture. Depending on the goals of the NAPL movement evaluation, different questions from the ones presented in Fig. 2 could be posed that are tailored to site-specific conditions. Fig. 2 also provides guidance on the types of laboratory tests, calculation methods or field data that will be useful in this evaluation. The evaluation methodologies outlined in Fig. 2 will help answer the key question of whether the NAPL in the sediment can migrate upward toward sensitive receptors (for example, benthic organisms in the biologically active zone of the sediment). Note that Steps 1 and 2 outlined in Fig. 2 concern NAPL mobility evaluation at the pore scale, while Steps 3 through 6 concern NAPL migration evaluation at the NAPL body scale.

5.4 Typically, the first step in a NAPL movement evaluation is to evaluate if the NAPL is mobile at the pore scale. NAPL mobility at the pore scale requires collecting undisturbed sediment samples and performing laboratory tests. This involves identifying the sediment intervals to obtain samples from cores for the NAPL movement evaluation. Examples of commonly used field screening methods for this task are presented in Table 2.

5.5 In general, sediment cores should be collected using methodologies that minimize disturbance of the sediment. It is

TABLE 1 Key Characteristics for Different NAPL Emplacement Mechanisms

Emplacement Condition	Emplacement Mechanism		
	Advective	OPA Deposition	DNAPL Surface Flow
Source	Directly related to upland source	Not physically connected to upland discharge source	Directly related to upland discharge source
Extent	Spatially limited; typically located along shoreline	Can be spatially large (many hectares) and found far from shoreline	Typically located along shoreline; can move farther from shoreline in some circumstances
NAPL Location in Strata	NAPL typically found in sand and more permeable strata	NAPL typically disconnected at pore scale; present throughout the sediment	DNAPL is the matrix, with solid grains embedded within and surrounding this matrix



NOTE 1—Each line indicates an evaluation is performed.

FIG. 1 General NAPL Movement Evaluation Framework

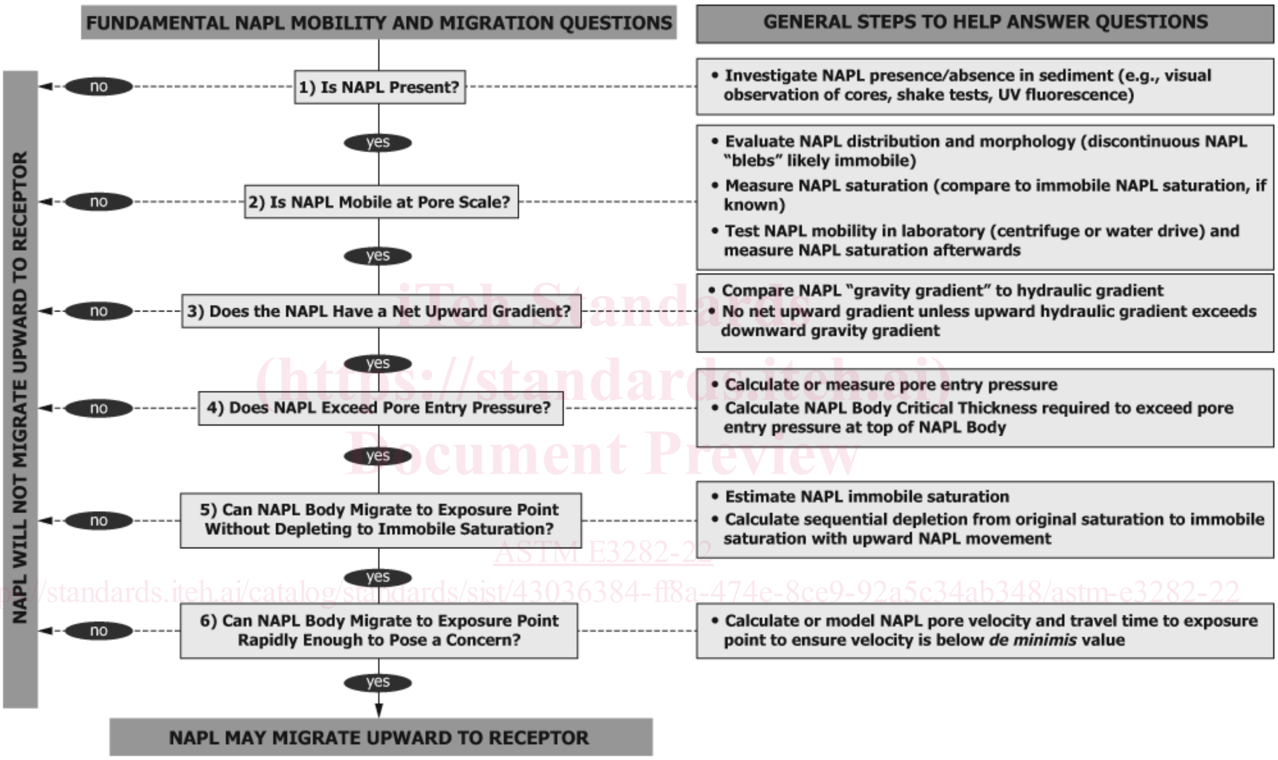


FIG. 2 Example NAPL Movement Investigative Process

good practice to take multiple co-located cores from each sampling station for the NAPL movement evaluation. One of these cores can be used for field screening, to determine if NAPL is present or absent at this sampling station—and to provide qualitative information on the degree of NAPL presence in various intervals of this core. Laboratory tests and field observations used to evaluate NAPL mobility at the pore scale are presented in Table 3.

5.6 If NAPL is demonstrated to be immobile at the pore scale at a particular location and depth, the evaluation is complete at that location and depth, because NAPL that is immobile at the pore scale (particularly if demonstrated to be immobile under conservative testing conditions) cannot be migrating and must be stable at the NAPL body scale. Laboratory NAPL mobility tests can be performed under a variety of applied hydraulic gradients in an attempt to mobilize NAPL from the sediment. To help correlate the laboratory testing to field conditions, the hydraulic gradient applied during pore-scale laboratory NAPL mobility testing should be equal to or greater than (that is, more conservative) those observed or reasonably anticipated under field conditions.

5.7 Unlike upland sites where numerous studies have allowed literature values to be developed, there is currently insufficient data to develop similar consensus literature values for immobile saturation in sediment. The immobile saturation values must currently be determined on a site-specific basis, established by the greatest measured NAPL saturation of site samples exhibiting immobility at the pore scale in laboratory testing. Immobile saturation values can vary with pore size distribution, density, organic content, and NAPL properties. If

TABLE 2 Common Screening Methods for Identifying Sediment Intervals for NAPL Movement Evaluation

Evaluation Methodology	Application	Test Method
Visual Observations	Identify presence/absence of NAPL in core intervals	Appendix X1 of Guide E3281
Shake Test	Identify presence/absence of NAPL in core intervals	Appendix X2 of Guide E3281
UV Light (Core Photography)	Confirm presence/absence of NAPL in core intervals and identify apparent maximum NAPL saturation interval for NAPL movement evaluation	Section 3.4.1 of Ref. **(6)**
LIF	Confirm presence/absence of NAPL in core intervals and identify intervals where NAPL fluorescence appears elevated; these intervals can be used in the NAPL movement evaluation. NAPL must contain polycyclic aromatic hydrocarbons (PAHs) for LIF to be applicable. LIF can be performed in situ or *ex situ*. LIF can be performed on DART[A] rods.	N/A
Hydrophobic Dye Test (NAPL FLUTe[B])	Identify presence/absence of NAPL in core intervals	N/A

[A] Trademarked by Dakota Technologies. http://www.dakotatechnologies.com/products/darts
[B] Trademarked by Flexible Liner Underground Technologies.

Abbreviations:
LIF = laser-induced fluorescence
N/A = not applicable

TABLE 3 Example Pore-Scale NAPL Mobility Evaluation Methodologies

Evaluation Methodology	Application	Emplacement Mechanism			Test Methods	Further Details
		Advective Flow	OPA Deposition	DNAPL Flow		
Laboratory Centrifuge Testing	Determines if NAPL is expressed from a core sample under very conservative conditions, at gradients much greater than the maximum measured or expected in the field. If no NAPL is expressed, the NAPL is immobile at the pore scale. If NAPL is expressed, it may be mobile at the pore scale. This documents potential mobility, but further assessment is needed to evaluate mobility under field conditions.	X	X	X	D6836	Section 7
Laboratory Water Drive Testing	Determines if NAPL is expressed from a core at a conservative vertical gradient, greater than the maximum measured or expected in the field. If NAPL is not expressed, the NAPL is immobile at the pore scale. If NAPL is expressed, it may be mobile at the pore scale under field conditions.	X	X	X	D5084	Section 8
NAPL Saturation	If the NAPL saturation in sediments is less than the site-specific immobile saturation, then the NAPL is immobile at the pore scale. If the NAPL saturation is greater than the immobile saturation, then the NAPL may be mobile.	X	X	X	Section 4.3 of Ref **(6)**	5.7
NAPL Presence in Well or Piezometer	If NAPL consistently accumulates in a monitoring well or piezometer installed in the sediment within a water body, the NAPL is mobile at the pore scale. If no NAPL accumulates, the NAPL is likely immobile at the pore scale.	X	X	X	N/A	10.3

Abbreviations:
N/A = not applicable
X = applicable

the NAPL saturation in sediment is greater than the site-specific immobile saturation values, it is potentially mobile at the pore scale. Once laboratory mobility testing has been performed on selected sediment samples from the site, the results (mobile or immobile) can be compared to the initial NAPL saturation results for the samples. There may be a NAPL saturation value below which the samples are immobile—and above which laboratory testing indicates they are potentially mobile. This threshold could allow estimation of the maximum immobile NAPL saturation value for the sediment. This threshold may be a range of values, rather than a single value, due to sediment and NAPL heterogeneity. For other samples taken at the site, this immobile NAPL saturation value may be useful to provide a basis of comparison to evaluate whether the NAPL in the sample is mobile at the pore scale.

5.8 If NAPL is demonstrated to be mobile at the pore scale during laboratory testing with a hydraulic gradient greater than those observed or reasonably anticipated in the field, then the stability of the NAPL body is uncertain and the evaluation must be continued. NAPL body stability (or migration) is commonly evaluated using the methodologies presented in Table 4. NAPL body migration evaluations consider in situ field conditions (for example, calculation of vertical gradients, NAPL physical properties, and sediment physical property measurements). If mathematical analysis is conducted, then site-specific parameter input values can be obtained from the results of the pore-scale mobility tests and from additional laboratory analyses (for example, NAPL fluid properties such as density, viscosity, and interfacial tension). A summary of commonly used laboratory testing methods applied in NAPL movement evaluations and a brief synopsis of each test method are presented in Appendix X1.

5.9 Once the status of the NAPL body (that is, stable or migrating) has been demonstrated, the NAPL movement evaluation is complete.

6. Tiered and Weight of Evidence NAPL Movement Evaluation Approaches

6.1 If NAPL is present in sediment, determining whether NAPL is mobile at the pore scale or migrating at the NAPL body scale is an important component of the site characterization process and subsequent development of a CSM. Conceptually, understanding the movement of NAPL requires an evaluation of the chemical and physical characteristics of the NAPL, as well as overall site conditions. A single test cannot necessarily determine whether NAPL is mobile or migrating, so tiered or WOE assessment approaches, relying on best professional judgment, are often needed. Deterministic analyses lend themselves to a tiered approach, but do not preclude a WOE evaluation. Table 3 and Table 4 summarize the LOEs (that is, evaluation methodologies) detailed in Sections 7 – 10, as well as how each could support an evaluation to determine if NAPL is mobile at the pore scale or

TABLE 4 Example NAPL Body-Scale Migration Evaluation Methodologies

Evaluation Methodology	Application	Emplacement Mechanism			Test Methods	Further Details
		Advective Flow	OPA Deposition	DNAPL Flow		
Net Vertical Gradient (where sediment–water interface is the exposure route of concern)	If the net vertical gradient (considering the gradient due to gravity and the hydraulic gradient) is net downward, NAPL cannot migrate upward to the sediment–water interface. Vertical gradients can vary temporally and can reverse in some instances. Hence, a number of net gradient determinations under different conditions (for example, different seasons, different points in the tidal cycle) may be required to demonstrate that the net gradient is downward most (if not all) of the time.	X	X	X	N/A	9.4, Appendix X7
NAPL Body Critical Thickness	To have sufficient NAPL capillary pressure at the top of the NAPL body to exceed the pore entry pressure of the overlying sediment, the NAPL body must be thicker than a certain critical value (which can be calculated and compared to field observations).	X	Y	X	N/A	9.6
NAPL Migration Distance Prior to Depletion to Immobile Saturation	Migrating NAPL leaves NAPL behind at immobile saturation, so that as NAPL moves, less NAPL mass is contained in the migrating front. Eventually, the NAPL mass in the migrating front decreases to the point of immobile saturation and migration ceases. If this occurs before the NAPL reaches a receptor, it will not be able to migrate to that receptor.	X	Y	X	N/A	9.7
NAPL Velocity	If the NAPL velocity to a potential receptor (for example, surficial sediment), is below a de minimis threshold (this depends on the distance to the receptor), the NAPL body is stable. A NAPL velocity less than the threshold translates into a very long travel time before the NAPL could potentially reach any receptor.	X	Y	X	N/A	9.8

Abbreviations:
N/A = not applicable
X = applicable
Y = applicable for partially encapsulated OPAs

migrating at the NAPL body scale. Guidelines for integrating these LOEs are described in this section, using both tiered and WOE approaches.

6.2 *Tiered Evaluation Approaches:*

6.2.1 The evaluation of NAPL movement may be based on a tiered (for example, decision-tree approach), similar to risk-based approaches associated with water quality assessment guidelines. Tiered approaches to environmental evaluations are widely accepted by industry and the professional community (**7**). The tiered evaluation generally involves three or more tiers (that is, levels), which enables the assessment to match variations in data availability, site complexity, and study objectives. A tiered approach to NAPL movement evaluation relies on sequential evaluations in tiers of increasing complexity.

6.2.2 A tiered approach allows simple cases to be completed relatively quickly and at lower cost, whereas more complex cases can be completed with a greater (but more efficient) use of resources. Tier 1 often consists of evaluations of field observations or binary field tests. Evaluations based on laboratory testing; detailed analysis of field or laboratory data; or the calculation of critical values are typically associated with Tier 2 (or greater). Tier 1 evaluation methods are generally low in cost, easy to perform, and provide qualitative or quantitative information about movement; they tend to be overly conservative and protective of project goals. Tier 2 (or greater) evaluation methods provide greater specificity and more quantifiable/calculable results, but they are often more expensive and time consuming than Tier 1 methods. When the evaluations within a specific tier are complete and the potential for NAPL movement cannot be rejected, then the next tier is performed (**8**). If NAPL movement is ruled out in a tier, then performing the following tiers is not necessary—the evaluation is complete.

6.2.3 For NAPL movement in sediment evaluations, there is no industry standard tiered approach. An illustrative example of a tiered approach to determine if NAPL is mobile at the pore scale at a site—and if it is, if the NAPL is migrating toward a receptor—is presented in Appendix X2. Case studies demonstrating the use of this illustrative tiered approach are presented in X3.2 and X3.3.

6.3 *Weight of Evidence Evaluation Approaches:*

6.3.1 WOE analysis is a data and information integration process that can be used for NAPL movement evaluations in sediment, where multiple measures (for example, analytical data, site history, visual observations) can be used as individual LOEs to assess the probability of NAPL mobility or migration. A discussion of the use of LOEs in WOE analysis is provided elsewhere (**9**). Relying on multiple LOEs using commonly available data provides an effective method to assess NAPL movement.

6.3.2 It is critical that stakeholders approach NAPL movement evaluations recognizing that there may be unique and challenging sediment management conditions at every site and appropriate site-specific metrics must be evaluated to determine if management goals are achievable. The process of weighing the evidence amounts to determining the conclusion best supported by the individual LOEs (**10**), with conclusions based (in part) on applying best professional judgment.

6.3.3 Once it has been determined that NAPL is present in the sediment, the objectives for further investigation and potential remediation strategies can be established. Converging LOEs can be used to determine whether NAPL is mobile on the pore scale or is migrating or stable at the NAPL body scale. In this instance, a WOE approach for NAPL mobility or migration can be used that is based on the evaluation metrics presented in Table 3 and Table 4. Based on site conditions and the potential for performing field investigations, a number of LOEs may be selected from the different field methods and desktop calculations. The LOEs used in the WOE can be equally weighted, or a decision analysis approach can be used, where different LOEs are unequally weighted in the WOE.

6.3.4 Any of the respective LOEs may lead to the conclusion that NAPL is mobile at the pore scale (a positive determination) or immobile (a negative determination). However, if the primary LOE suggests that NAPL is immobile, then the determination of mobility turns to a WOE approach, where additional LOEs combine to confirm a negative determination. Alternatively, a number of positive determinations may outweigh the negative determination, if the positive LOEs cannot be explained without the presence of mobile NAPL. A similar rationale can be used to evaluate if NAPL is migrating or stable at the NAPL body scale, using a WOE approach. Because a WOE is typically structured to answer a single question (for example, is the NAPL mobile at the pore scale), it is simpler to use one WOE to determine if NAPL is mobile at the pore scale, then a second WOE to determine if NAPL is migrating at the NAPL body scale. Depending on project goals, it might be decided to take a tiered approach to determine pore-scale mobility and a WOE approach to determine NAPL body-scale migration, or vice versa.

6.3.5 For NAPL movement in sediment evaluations, there is no industry standard WOE approach. An illustrative example of a WOE approach to determine if NAPL at a site is mobile at the pore scale is presented in Appendix X2. An illustrative example of another WOE approach to determine if NAPL at a site is migrating at the NAPL body scale is also presented in Appendix X2. A case study demonstrating the use of both of these illustrative WOE approaches is presented in X3.4.

7. Centrifuge Test Methods

7.1 *General Overview of Centrifuge Test Methods:*

7.1.1 Centrifuge test methods evaluate the potential for NAPL movement at the pore scale under different pressure (that is, gradient) conditions.

7.1.2 Centrifuge technology involves spinning a sediment core sample, such that the angular velocity induces a negative pressure that then displaces fluids from the pore network. By measuring the relative fluid content at various displacement pressures (that is, matric potentials resulting from the applied centrifugal forces), a capillary pressure curve is produced. From these measurements a number of physical properties related to fluid distribution, content, retention, and movement can be determined. The application of centrifuge technology is described in Test Methods D425 and D6836, as well as in

Section 4 of Ref. (**6**). Environmental applications of centrifuge technology to evaluate NAPL movement in porous media have been reported by Soga et al. (**11**), Brady and Kunkel (**12**), and Johnson et al. (**13**). Appendix X4 provides further information on the use of centrifuge technology in pore-scale NAPL mobility testing; it also provides methodologies for conversion from centrifugal force (in G) to the hydraulic gradient and capillary pressure (in psi) experienced by the sample.

7.1.3 Centrifuge applications for NAPL characterization in sediments have been limited. Following the general procedures of Brady and Kunkel (**12**), Johnson et al. (**13**) conducted NAPL mobility analyses of IDN sediments.

7.1.3.1 Concerns exist regarding the application of centrifuge technology in soils and sediments. Soga et al. (**11**) reported several effects induced by centrifuging NAPL-containing soil samples, including *(1)* a change in pore size, due to compression of the sample by the increased gravity; *(2)* a decrease in contact angle between air and water, due to the rapid and large acceleration; and *(3)* changes in contact angle or immobile saturation with fluid velocity. Given the lower degree of consolidation of sediments relative to soils, these effects may also occur in NAPL-containing sediments. Despite these concerns, forces applied through centrifugation outweigh the factors discussed above, so centrifuge technology provides a useful conservative measure of potential NAPL mobility in sediment samples on an accelerated time scale compared to the field.

7.2 To obtain the best quality results, samples provided for testing should be representative of field conditions and compatible with the testing apparatus.

7.2.1 Undisturbed samples must be obtained in core sleeves that support testing in the apparatus selected for testing and that are compatible with both the anticipated sample handling (for example, frozen versus unfrozen) and NAPL composition. Details of sediment sample collection and handling should be discussed with the testing laboratory while planning for the field event. Appendix X5 presents guidance on how to properly process field samples in the laboratory to obtain samples for centrifuge testing.

7.2.2 In the laboratory, undisturbed samples are inserted into centrifuge cups and then spun for a period of time at a given spin rate to produce a defined negative displacement pressure at a controlled temperature. Fluids produced are collected and the volumes measured. Bulk density and porosity are subsequently measured on the sample. Immediately after completion of the centrifuge run, the final volume or mass of fluids produced is recorded and the sample is weighed and placed in a Dean-Stark extraction vessel, where residual fluid saturations are determined. Less commonly, a Karl Fischer titration can be used (Section 4.4.1 of Ref. (**6**)).

7.2.3 The initial NAPL and water saturations are calculated through mass balance by the laboratory. The initial NAPL saturation is determined by adding the amount of NAPL produced during the centrifuge test to the residual oil volume and dividing the sum by the sample pore volume. The initial water saturation is calculated by adding the centrifuge test-produced water to the residual water volume and dividing the sum by the sample pore volume. Centrifuge test-produced water is calculated by subtracting sample native weight from the post-centrifuge test sample weight and adjusting for any NAPL released.

7.2.4 Centrifuge methods have been historically used to measure NAPL mobility in soils under very conservative test conditions, at hydraulic gradients much greater than could ever be observed under current or reasonably anticipated field conditions. This practice has utilized a displacement pressure of 1 000 times the force of gravity (1 000 G) for 1 h (**12**). The application of such a high displacement pressure is not recommended for sediments, because these forces are much greater than could be achieved in the field and may produce extreme compression of the sample for most sediments.

7.2.5 To more realistically assess NAPL mobility, it is recommended that induced centrifuge displacement pressures be conducted at conditions more indicative of field conditions (see Appendix X4). These conditions are generally less than 20 psi. Step-based centrifuge tests, where the displacement pressure is increased incrementally at discrete intervals, provide a comprehensive suite of measurements of fluid drainage (NAPL and water), so this reflects the evacuation of pore fluids from decreasing pore opening sizes. From this type of centrifuge test, the potential mobility of the NAPL can be evaluated with respect to water displacement and the location of the NAPL within the sediment pore structure can be ascertained. A case study demonstrating the application of this type of centrifuge testing in a NAPL emplacement evaluation is presented in X3.1.

8. Water Drive Test Methods

8.1 Water drive tests can be used to evaluate NAPL mobility at the sediment pore scale under defined laboratory conditions (**6**). These are modified permeameter tests, based on established geotechnical methods for soils. During a water drive test, an undisturbed sediment sample is placed under a practitioner-defined vertical hydraulic gradient, where the water is introduced to the sample in an upflow configuration. Effluent from the sample is monitored for signs of expressed NAPL, while parameters such as inlet pressure, outlet pressure, and applied water flow rate are recorded as a function of time, to define the conditions of testing and allow calculation of the effective hydraulic conductivity of the sediment sample.

8.1.1 If NAPL is observed (that is, if NAPL is observed in the fluids expressed from the sample at any point in the test), additional water may be applied to the sample until no additional NAPL is expressed (typically two pore volumes of NAPL-free water). When the purpose of the test is only to determine if NAPL is mobile or immobile under the test condition, the test is terminated at this point.

8.1.2 If NAPL is not observed (that is, NAPL is not observed in the fluids expressed from the sample after two pore volumes of water have been passed through it), a stronger vertical hydraulic gradient may be applied to investigate if NAPL can be mobilized under more severe conditions.

8.1.3 Once all mobile NAPL under the specified test conditions has been removed from the sediment sample, the sample is analyzed (for example, Dean-Stark) to quantify the amount of NAPL and water remaining in the sample, in order to calculate the initial NAPL and water saturations. This aids in the establishment of threshold criteria for NAPL mobility under the given test conditions.

8.2 Apparatuses used for water drive testing are distinguished from one another based on the cell holding the sediment sample within the test apparatus. These apparatuses and their general functioning are based on geotechnical methods for soil permeability testing, which employ rigid wall (Test Method D5856) or flexible wall (Test Method D5084) test cells. The rigid wall tests hold the sediment sample within a solid wall permeameter ring. The flexible wall permeameter apparatus surrounds the sediment sample with a latex rubber membrane that is placed in a pressurized triaxial cell to simulate in situ confining pressures.

8.2.1 Both water drive methods result in the same measured properties; similar results should be obtained when sample handling retains the undisturbed nature of the sediment sample.

8.2.2 A comparison of the advantages and disadvantages of the two water drive test methods is provided in Table 5.

8.3 Application of water drive testing to evaluate NAPL mobility in sediment has been reported by Niemet et al. (**14**). Appendix X6 provides details on test apparatuses used and guidance for test design.

8.4 To obtain the best quality results, samples provided for testing should be representative of field conditions and compatible with the testing apparatus. Appendix X5 presents guidance on how to properly process sediment cores in the laboratory to obtain samples for water drive testing.

8.4.1 Undisturbed samples must be obtained in core sleeves that support testing in the apparatus selected for testing and that are compatible with both the anticipated sample handling (for example, frozen versus unfrozen) and NAPL composition. Details of sediment sample collection and handling should be discussed with the testing laboratory while planning for the field event.

8.4.2 Site water should be obtained to be used in the testing, if possible. This is especially important in saltwater environments, where the greater ionic strength of the water will more substantially affect the interaction of NAPL with its environment. Consideration should be given to degassing the site water to avoid bubble formation in the sample, which may affect hydraulic conductivity measurements.

8.5 While planning the test design, it is important to consider what vertical hydraulic gradients should be tested to be representative of site conditions (including a factor of safety) and the number of pore volumes of water that should be pushed through the sample to achieve test objectives (for example, demonstration that conditions of NAPL immobility have been reached).

8.5.1 Vertical hydraulic gradients for testing should consider site conditions (gradients and groundwater velocities) or sample permeability. Prior to testing, hydraulic analyses are conducted to define the representative site conditions. Specifically, the flux is determined from measured or calculated groundwater velocities. Due to uncertainties, the flux is generally expressed as a range of values, rather than a single value. At least two gradients are typically tested for each sample, starting with the lowest gradient and sequentially increasing to the highest gradient. The target lower flux bound should be as representative as possible of current or reasonably anticipated field conditions, and the target upper flux bound should consider the potential maximum flux conditions at the site, plus an increment of flux to address uncertainty.

8.5.1.1 The hydraulic gradient (i) is proportional to the pressure drop across the core segment.

$$i = \frac{\Delta h}{L_f} \tag{1}$$

where:

i = the hydraulic gradient, dimensionless,
Δh = difference in hydraulic head across the specimen, m or cm of water, and
L_f = final length of the specimen along the path of flow, m or cm.

8.5.1.2 The pressures in the test apparatus are measured with a pressure transducer, manometer, or other suitable device

TABLE 5 Comparison of Water Drive Test Methods

Method	Advantages	Disadvantages
Rigid Wall	• Less complicated sample preparation and testing procedure. • This test method has a longer history than the flexible wall test, so there is a longer track record of success with this method. • More suitable for relatively unconsolidated sediments, because they are more easily placed in the apparatus without disturbing the sediment matrix than flexible wall cell.	• Potential for water to channel along the sidewall of the permeameter cell and not flow through the bulk of the sediment sample. • If wall leakage cannot be prevented, the results may overestimate permeability and NAPL mobility.
Flexible Wall	• Reduces the potential for sidewall channeling compared to rigid wall cell.	• Relatively unconsolidated sediments are difficult to place in the apparatus without disturbing the sediment matrix. • Relatively unconsolidated sediments could potentially deform in the flexible cell if the consolidation pressure exceeds in situ consolidation pressure. • More complicated sample preparation and testing procedure. • More limited commercial offerings of this method compared to rigid wall test.

in the permeant water (that is, water that passes through the sample) immediately upstream and downstream of the sample, if not open to the atmosphere. In tests using an upflow configuration, Δh is calculated as the difference between the total back pressure of the system (measured immediately upstream of the sample) and the hydrostatic head. The hydrostatic head pressure will change slightly as water accumulates in the upper reservoir, but this effect is negligible in most cases, because the change is significantly less than Δh.

8.5.1.3 By Darcy's law (Eq 2), Δh is proportional to the flow rate of the permeant water through the test specimen.

$$\Delta h = \frac{\Delta V L_f}{A \Delta t K} \tag{2}$$

where:

ΔV = volume of flow, taken as the average of inflow and outflow, m^3 or cm^3 .
A = cross-sectional area of the specimen, m^2 or cm^2,
Δt = interval of time over which the flow ΔV occurs, s, and
K = hydraulic conductivity, m/s or cm/s.

8.5.1.4 Typically, target hydraulic gradients are provided to the laboratory, and laboratory personnel must determine the appropriate flow rate to apply to the sample to obtain the desired gradient. When planning for testing, an initial estimate of hydraulic conductivity based on a known sediment texture may be used to estimate the flow rate that will be used to achieve the targeted hydraulic gradients and subsequently the duration of each test. Prior to testing on the targeted mobility sample, the target flow rates and the associated gradients should be validated on a pre-test sample (that is, one not selected for mobility testing but that has similar properties to the selected samples) from the site.

8.5.1.5 If the test durations targeting site hydraulic gradients are anticipated to be impractically long given laboratory or schedule constraints, desired observation intervals, or effluent sampling, then target flow rates may be provided and the associated gradients calculated. These results will be conservative indicators for NAPL mobility potential.

8.5.1.6 Test apparatuses may have limitations on the amount of pressure that can be applied to the sample, which may limit the range of hydraulic gradients that can be tested. Consult with laboratory personnel to determine the range of gradients possible for testing with the anticipated site sediments, especially if the hydraulic conductivity of the sediment sample is relatively low (that is, $K < 1 \times 10^{-6}$ cm/s).

8.5.2 At least two pore volumes should be pushed through the sample to determine the potential for NAPL mobility at the test gradient, but greater volumes may be used to achieve test objectives (for example, depleting mobile NAPL in the sample or providing sufficient expressed NAPL for sampling and laboratory analysis). The test duration for each sample should be considered when planning the test approach and number of samples to be tested to meet test objectives.

8.5.3 Additional guidance and test design examples for both rigid wall and flexible wall tests are provided in Appendix X6, as well as in Test Methods D5084 and D5856.

9. Calculation Methods for Potential Vertical Movement of NAPL

9.1 This section focuses on methods to quantify NAPL migration due to advection; these methods are not applicable in cases where the NAPL is immobile at the pore scale.

9.2 NAPL that has been historically emplaced advectively in sediment was driven by horizontal hydraulic gradient beneath the upland (Appendix X1 of Guide E3248). Beneath the water body, the hydraulic gradient is predominantly vertical.

9.2.1 Vertical NAPL migration potential is of particular interest in sediment systems, because the potential for exposure to receptors increases near the sediment surface, as described in 4.4. Therefore, whether NAPL in deeper sediments can migrate upward toward surficial sediment is particularly important. Less commonly, downward NAPL movement to a receptor (for example, a lower aquifer) is of interest at sediment sites.

9.3 NAPL mobility calculations depend on hydraulic gradient, density-driven gradient, pore fluid saturation, capillary pressure, viscosity, interfacial tension, relative permeability, and wettability. These concepts are described in detail in reference works such as Ref. (**1**), Pankow and Cherry (**15**), and Ref. (**3**). Current understanding and application of these concepts for LNAPL have been summarized in Ref. (**2**).

9.3.1 Collectively, these parameters control NAPL mobility at the pore scale due to advective processes in sediment; their definitions are provided in Section 3.

9.4 *NAPL Density and Vertical Hydraulic Gradient:*

9.4.1 An initial calculation to evaluate the potential for vertical NAPL migration can be performed based on the magnitude of the gravitational and hydrodynamic driving forces. As detailed in Appendix X7, the net vertical gradient can be calculated as follows:

$$i_{nv} = \frac{\rho_n - \rho_w}{\rho_w} + \frac{dh_w}{dz} \tag{3}$$

where:

i_{nv} = net vertical gradient, dimensionless,
ρ_w = water density (accounting for salinity), g/cm^3,
ρ_n = NAPL density, g/cm^3,
dh_w = hydraulic head difference used in vertical hydraulic gradient calculations, cm of water, and
dh_w/dz = vertical hydraulic gradient associated with groundwater flow (positive for downward flow and negative for upward flow), dimensionless.

9.4.2 The first term on the right side of Eq 3 is the hydraulic gradient due to gravity (**15**) and represents the driving force related to the NAPL density in an otherwise water-saturated medium.

9.4.3 If the hydraulic gradient due to gravity and hydraulic gradient associated with groundwater flow act in opposite directions, the term that is greater in magnitude will determine the direction of i_{nv} (upward or downward). For non-wetting NAPL to migrate upward within sediment, i_{nv} must be negative. If i_{nv} is positive, a non-wetting NAPL may migrate downward, but it cannot migrate upward. In addition, even if

i_{nv} is negative, NAPL will not migrate upward if the overlying material lacks NAPL and the NAPL pressure cannot overcome the pore entry pressure of the overlying sediment.

9.5 *Pore Entry Pressure:*

9.5.1 Capillary forces occur due to physical interaction between solids and liquids. In porous media, such as sediment systems, these forces generally restrict the pore-scale mobility of non-wetting fluids. In saturated media (such as sediments), water is typically the wetting fluid and NAPL is the non-wetting fluid (**1**); the attraction between water and the solid particles is greater than the attraction between the NAPL and solid particles, so water preferentially covers the solid surfaces. Wettability may be affected by the salinity of the porewater; when salinity increases, the wettability of the NAPL phase typically increases (**16**).

9.5.2 When NAPL is the wetting phase, it wicks into the porous medium (pulled by capillary suction). However, when water is the wetting phase, displacement of water by NAPL requires force. The capillary pressure that is required for a NAPL to displace water within a porous medium is known as the pore entry pressure. Pore entry pressure is used to evaluate whether a NAPL body has sufficient vertical thickness to migrate upward within sediment as discussed in 9.6.

9.5.3 Pore entry pressure can be calculated using the Laplace equation:

$$P_{e(nw)} = \frac{2\sigma_{nw}\cos\varphi}{r\rho_w g} \qquad (4)$$

where:

$P_{e(nw)}$ = pore entry pressure for NAPL in a water-filled pore (expressed as an equivalent head of water), cm of water,
σ_{nw} = interfacial tension between NAPL and water, dyne/cm,
φ = contact angle between NAPL–water interface and the water–solids interface, degrees,
r = radius of the water-filled pore, cm,
ρ_w = water density, g/cm^3, and
g = gravitational constant, 980 cm/s^2.

9.5.4 Pore entry pressure increases with increasing NAPL–water interfacial tension and decreasing pore size.

9.5.5 A practical method to determine NAPL entry pressure is to collect an intact sediment sample and submit it to a geotechnical laboratory for capillary pressure testing; the centrifuge method discussed in 7.1.2 is an acceptable method of testing (subject to the limitations discussed in 7.1.3.1). Capillary pressure testing determines the force required for air, which is a non-wetting fluid, to displace water and NAPL from the sample. The data show a relationship between the applied air pressure and how much water was displaced from the sample, which corresponds to the distribution of pore diameters within the sediment. The test results indicate the critical air pressure that must be achieved for air to begin displacing water. This critical pressure is the air entry pressure, which can be converted (scaled) to the equivalent NAPL/water displacement head based on the proportionality of interfacial tension and pore entry pressure:

$$P_{e(nw)} = \left(\frac{\sigma_{nw}}{\sigma_{aw}}\right) h_{c(aw)} \qquad (5)$$

where:

σ_{aw} = air–water interfacial (surface) tension, dyne/cm, and
$h_{c(aw)}$ = capillary pressure for air displacing water (expressed as an equivalent head of water), cm of water.

9.5.6 Another alternative is to estimate pore entry pressure based on physical properties of the sediment and NAPL. One example is an empirical relationship (**15**):

$$P_{e(nw)} = 9.6(\sigma_{nw}/\sigma_{aw})(K_w/n)^{-0.403} \qquad (6)$$

where:

K_w = water-saturated hydraulic conductivity, cm/s, and
n = porosity of the porous medium, dimensionless.

9.5.7 In stratified geologic systems with K_w and n variations between stratigraphic layers, NAPL in a coarse-grained unit may not be capable of overcoming the greater pore entry pressures of an overlying finer-grained unit; in this case, the NAPL is more likely to migrate farther laterally within the coarse-grained unit than penetrate upward into the finer-grained unit. Thus, the pore entry pressure is an important variable in the stability of a NAPL body and can prevent NAPL from migrating upward within sediment in many cases.

9.6 *Critical NAPL Layer Thickness:*

9.6.1 Upward mobility of non-wetting NAPL in subaqueous sediment depends on the NAPL body exerting enough capillary pressure to overcome the entry pressure of the adjacent overlying porous medium. Based on principles presented elsewhere (**15, 17**), if the net vertical gradient (i_{nv}) is negative, then the capillary pressure at the top of the NAPL body increases with larger contiguous NAPL thicknesses. At a critical vertical thickness (or height) of NAPL, the capillary pressure at the top of the NAPL body is great enough to exceed the pore entry pressure of the porous medium above it, thereby allowing upward NAPL flow. The same principle applies to horizontal NAPL movement, but the pore entry pressure of interest in that case is that of the adjacent porous medium at the same elevation as the NAPL body.

9.6.2 The critical NAPL thickness (h_n) required for vertically contiguous mobile NAPL to reach the pore entry pressure at the base of the NAPL body is presented in Eq 7 (based on Payne et al. (**17**)):

$$h_n = \frac{P_{e(nw)}}{\frac{\rho_n - \rho_w}{\rho_w} + \frac{dh_w}{dz}} \qquad (7)$$

9.6.3 Similarly, the critical NAPL thickness (h_n) required for vertically contiguous mobile NAPL to reach the pore entry pressure at the top of the NAPL body can be calculated as follows:

$$h_n = \frac{P_{e(nw)}}{-\left(\frac{\rho_n - \rho_w}{\rho_w} + \frac{dh_w}{dz}\right)} \qquad (8)$$

9.6.4 The minus sign in the denominator of Eq 8 is necessary, because the net vertical gradient must be negative to produce an upward potential for NAPL movement.