

Designation: E3300 - 21

Standard Guide for NAPL Mobility and Migration in Sediment— Evaluating Ebullition and Associated NAPL/Contaminant Transport¹

This standard is issued under the fixed designation E3300; 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 addresses the processes that lead to (or influence) ebullition-facilitated nonaqueous phase liquid (NAPL)/contaminant transport, methods for quantifying that transport, considerations for sample timing, sampling procedures, and use of results in extrapolating an annual ebullition-facilitated NAPL/contaminant load to a site, or a portion of a site. This guide is not intended to address remediation of sites where ebullition-facilitated transport of NAPL/contaminants is occurring, fate and transport of contaminants subsequent to the ebullition transport mechanism, the measurement of contaminant concentrations within the gas bubbles, ebullition-associated human health and ecological risk, NAPL advection, or determining the depth of ebullition below the mudline. Additionally, gas transport without NAPL/ contaminants is possible in areas with gas generation and limited NAPL contamination of the sediment, which is covered in this guide. Ebullition should be evaluated at sites where sediment capping is anticipated.

1.2 The users of this guide should be aware of the appropriate regulatory requirements that apply to sediment sites where NAPL is present or suspected to occur. The user should consult applicable regulatory agency requirements to identify appropriate technical decision criteria and seek regulatory approvals, as necessary.

1.3 ASTM standard guides are not regulations; they are consensus standard guides that may be followed voluntarily to support applicable regulatory requirements. This guide may be used in conjunction with other ASTM guides developed for sediment programs. The guide supplements characterization and remedial efforts performed under international, federal, state, and local environmental programs, but it does not replace regulatory agency requirements.

1.4 The values stated in SI units are to be regarded as the standard. No other units of measurement are included in this standard.

1.5 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.

1.6 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
- E1689 Guide for Developing Conceptual Site Models for Contaminated Sites
- E1739 Guide for Risk-Based Corrective Action Applied at Petroleum Release Sites
- E2081 Guide for Risk-Based Corrective Action
- E2531 Guide for Development of Conceptual Site Models and Remediation Strategies for Light Nonaqueous-Phase Liquids Released to the Subsurface
- E2993 Guide for Evaluating Potential Hazard as a Result of Methane in the Vadose Zone
- E3163 Guide for Selection and Application of Analytical Methods and Procedures Used during Sediment Corrective Action
- E3248 Guide for NAPL Mobility and Migration in Sediment – Conceptual Models for Emplacement and Advection

3. Terminology

3.1 Definitions:

3.1.1 *biogenic, adj*—resulting from the activity of living organisms (Guide E2993).

3.1.2 *contaminant*, *n*—substance not normally found in an environment at the observed concentration (Guide E2993).

¹ This guide is under the jurisdiction of ASTM Committee E50 on Environmental Assessment, Risk Management and Corrective Action and is the direct responsibility of Subcommittee E50.04 on Corrective Action.

Current edition approved Sept. 15, 2021. Published October 2021. DOI: 10.1520/E3300-21.

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.

3.1.3 *flux*, *n*—mass crossing a unit area per unit time in any phase (for example, LNAPL, dissolved-phase, vapor-phase) (Guide E2531).

3.1.3.1 *Discussion*—For ebullition, the unit area of interest is the sediment-water interface.

3.1.4 *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 (Guide E3248).

3.1.5 *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 (Guide E3248).

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

3.1.6.1 *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]).

3.1.7 *sediment*—a matrix of porewater and particles including gravel, sand, silt, clay, and other natural and anthropogenic substances that have settled at the bottom of a tidal or nontidal body of water (Guide E3163).

3.2 Definitions of Terms Specific to This Standard:

3.2.1 *acetoclastic organisms*, *n*—microbial organisms that convert acetic acid to methane.

3.2.2 *acetogenesis*, *n*—the biological formation of acetic acid from carbon dioxide or organic acids.

3.2.3 *cone sampler, n*—a sampler that uses an inverted cone or funnel of sufficient size to trap and measure gas released from the sediment.

3.2.3.1 *Discussion*—The cone is typically connected to a frame for supporting the sampler during field deployment and provides additional volume for gas collection. The sampler can be positioned near the sediment surface or within the water column.

3.2.4 *corral sampler*, *n*—a sampler that consists of an inflatable boom to isolate the gas measurement area, with a thin film placed over the sampling area to trap gas bubbles released from the sediment.

3.2.5 *ebullition*, n—a process of gas (primarily methane) generation in sediments where the quantity of gas generated is sufficient for gas bubbles to nucleate, grow, fracture the sediment, and then escape into the overlying water body.

3.2.5.1 *Discussion*—Depending on the composition of a particular sediment, the gas bubbles generated and released by ebullition may strip constituents out of the sediment and transport these into the overlying water.

3.2.6 *ebullition active area, n*—a subarea within a larger ebullition study area where gas ebullition occurs consistently during an ebullition survey.

3.2.7 *ebullition rate, n*—the rate of volumetric gas production from the sediment, measured in micromoles of gas per unit surface area of sediment per unit of time.

3.2.8 *flux chamber*, *n*—a device with an isolation chamber that can trap gas bubbles rising through the water column.

3.2.8.1 *Discussion*—The isolation chamber is equipped with vent valve for sampling the headspace and measuring the volume of accumulated gases.

3.2.9 *hydrogenotrophic organisms*, *n*—microbial organisms that use molecular hydrogen as a metabolic energy source.

3.2.10 *labile organic matter; n*—carbon-based materials that can be consumed and broken down by microorganisms, with the typical eventual metabolic end products being methane or carbon dioxide, or both.

3.2.11 *mesophilic organisms*, *n*—microbial organisms that can grow at a moderate temperature range of 20 °C – 45 °C with an optimum growth temperature in the range of 30 °C – 39 °C.

3.2.12 *methanogenesis*, *n*—the generation of methane by microorganisms, typically through the consumption of labile organic matter (OM).

3.2.13 *methanotrophic organisms, n*—a group of microbial organisms that utilize methane as a carbon source.

3.2.14 *nucleation*, *n*—the initial formation of a separate gas phase bubble in a surrounding liquid that is supersaturated with that gas.

3.2.15 *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.

3.2.16 *seep*, n—a location that slowly releases small quantities of NAPL from sediments or other water interfaces

3.2.16.1 *Discussion*—Seeps differ from ebullition because the release of the NAPL from the sediments and the flux of the NAPL across the sediment-water interface occur without facilitation from gas bubbles. Seeps and ebullition can be coincident but they are fundamentally separate phenomena.

3.2.17 *sheen, n*—a silvery, rainbow, or dark rainbow film on the water surface.

3.2.18 *sheen blossom*, *n*—the emergence of NAPL transported by a gas bubble at the water surface followed by spreading of NAPL into a sheen at the air-water interface.

3.2.19 *tent sampler*, *n*—a square or rectangular frame covered by a thin film to trap gas bubbles.

3.2.19.1 *Discussion*—The film is equipped with a sampling port for sample collection and measuring the total volume of gas trapped by the sampler. The rectangular frame floats on the water surface and can move vertically with changes in water depth.

4. Significance and Use

4.1 Ebullition is ubiquitous in sediment and is primarily a significant concern when there is associated NAPL/ contaminant transport, resulting in exposure risk to humans, ecological receptors, or both. Ebullition may also be a concern when capping has been chosen as part of a site remedy.

4.2 Understanding the potential for ebullition-facilitated NAPL/contaminant transport in sediment is an important element of an overall conceptual site model (CSM) that forms

a basis for (1) evaluating if (and how) human and ecological receptors may be exposed to NAPL/contaminants, and (2) assessing remedial alternatives. In addition, demonstrating the potential for (and extent of) ebullition-facilitated transport of NAPL/contaminants in sediments to regulators and other stakeholders has been historically hampered by the lack of standardized terminology and characterization protocols. The complexity of ebullition-facilitated NAPL/contaminant transport in sediment, and the lack of agreed upon methods for analysis and interpretation of site data, has led to uncertainty in corrective action decision-making at sediment sites. This has sometimes resulted in misleading expectations about remedial outcomes. The ebullition-facilitated transport mechanisms for NAPL/contaminants in sediments are different from advective transport mechanisms in sediment or in upland environments, due to a variety of physical, geochemical, and biological differences, thus necessitating this guide.

4.3 This guide is intended to serve as a stand-alone document to consider conditions that are unique to ebullition and ebullition-facilitated NAPL/contaminant transport, as well as to complement other guides used for CSM development at contaminated sediment sites (Guides E1689, E1739, E2081, E2531, and E3248). This guide will aid users in understanding the unique and fundamental characteristics of sediment environments that influence the occurrence of ebullition-facilitated NAPL/contaminant transport. Understanding the site characteristics that influence ebullition-facilitated NAPL/contaminant transport within the sediment column will aid in identifying specific data requirements necessary to investigate these conditions, which will enable further refinement of the CSM and provide a sound basis for remedy decisions.

4.4 Ebullition-facilitated NAPL/contaminant transport is the primary transport mechanism that is addressed within this guide.

4.4.1 In addition to ebullition-facilitated NAPL/ contaminant transport, porewater advection may also facilitate NAPL/contaminant transport; however, this process is beyond the scope of this guide. Advective transport of NAPL in sediments is addressed in Guide E3248.

4.4.2 Processes associated with NAPL/contaminant transport due to erosion (for example, propeller wash) are not within the scope of this guide.

4.5 This guide identifies the relevant information necessary for a technically reliable and comprehensive CSM in support of the investigation or remediation of ebullition-facilitated NAPL/contaminant transport in sediments. It describes the conditions that lead to (or influence) ebullition-facilitated NAPL/contaminant transport, methods for quantifying the ebullition-facilitated NAPL/contaminant flux rate, considerations for field measurements, and use of field results in extrapolating the NAPL/contaminant flux rate. A technically reliable and comprehensive CSM will result in a more efficient and consistent investigation of ebullition-facilitated NAPL/ contaminant transport in sediments to support remedy decisions. This guide may also be beneficial for evaluating ebullition alone at sites (for example, as input into sediment cap design). 4.6 Many materials (for example, chlorinated solvents, petroleum products, and creosote) enter the subsurface as an immiscible liquid, known as NAPL, which may flow as a separate phase from water. NAPL can contain contaminants, such as polycyclic aromatic hydrocarbons (PAHs).

4.6.1 Sheens may be observed on the surface of the water body from sources other than ebullition, such as natural/ biogenic sheens, advective NAPL/contaminant transport, outfalls (for example, municipal and industrial), or vessel leaks. Identifying sources of sheens other than ebullition is not within the scope of this guide.

4.7 This guide assumes that a CSM has been developed that includes the nature and extent of NAPL/contaminants in sediment. This CSM would include an understanding of (1) the hydrological setting, (2) the physical and chemical characteristics of the sediment and water body, (3) the physical and chemical characteristics of the NAPL/contaminants, (4) mechanism(s) of NAPL/contaminant emplacement, (5) the physical extent of the NAPL/contaminant zone, and (6) the potential for human and ecological exposures to NAPL/ contaminants in sediment, or via NAPL/contaminant release to overlying surface water. The means and methods for collecting this information are not addressed in this guide.

4.8 This guide assumes that the user has developed a CSM that provides a framework for developing a conceptual model (CM) that is a component of the overall CSM, which addresses ebullition-facilitated NAPL/contaminant transport. This guide will help users understand the physical and chemical conditions and emplacement mechanisms that lead to (or influence) ebullition-facilitated NAPL/contaminant transport, as well as aid in prioritizing and executing methods for gathering field data and interpreting results to support the development of a CSM for the site.

4.8.1 The elements of the ebullition-facilitated NAPL/ contaminant transport CM describe the physical and chemical properties of the environment, the hydraulic conditions, the source of the NAPL/contaminants, and the nature and extent of the NAPL/contaminant zone. The CM is a dynamic, evolving model that will change through time as new data are collected and evaluated or as physical conditions of the site change due to natural or engineered processes. The goal of the CM is to describe the nature, distribution, and setting of the NAPL/ contaminants in sufficient detail, so that questions regarding current and potential future risks, longevity, and amenability to remedial action can be adequately addressed.

4.8.2 The elements for the ebullition-facilitated NAPL/ contaminant transport CM may include, but are not limited to: 4.8.2.1 Factors affecting the rate of gas production:

(1) Presence of microbial consortia capable of OM mineralization

(2) Presence of labile OM

(3) Geochemical conditions conducive to methanogenesis(4) Sediment temperature

4.8.2.2 Factors affecting the nucleation of gas bubbles, bubble growth and migration through the sediment column:

(1) Availability of nucleation sites

(2) Sediment properties (for example, tensile strength, grain size, porosity, bulk density, cohesion, and heterogeneity)

(3) Porewater properties (for example, gas concentrations, salinity, pH, and geochemistry)

(4) Environmental setting (for example, hydrostatic pressure, atmospheric pressure, and groundwater seepage)

4.8.2.3 Presence and extent of the NAPL/contaminant zone, including identification of where it is collocated with active ebullition zones.

4.8.2.4 Ebullition-facilitated NAPL/contaminant transport rates, including spatial and temporal variability:

(1) Screening-level evaluations

(2) Quantitative evaluations

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

4.9.1 Section 1: Scope;

4.9.2 Section 2: Referenced Documents;

4.9.3 Section 3: Terminology;

4.9.4 Section 4: Significance and Use;

4.9.5 Section 5: Fundamentals and Considerations During Development of a Conceptual Site Model

4.9.6 Section 6: Initial Screening for Gas Ebullition and Ebullition Flux Measurement;

4.9.7 Section 7: Gas Ebullition Measurement;

4.9.8 Section 8: Quantification of Ebullition-Facilitated Transport of NAPL/Contaminants;

4.9.9 Section 9: Field Considerations in the Measurement of NAPL/Contaminant Fluxes;

4.9.10 Section 10: Keywords;

4.9.11 Appendix X1: Organic Matter Degradation and Microbiology of Biogenic Gas Production in Sediments;

4.9.12 Appendix X2: Carbon Source Identification Using Radioisotope Analysis;

4.9.13 Appendix X3: Bench Scale Testing for Biogenic Gas; and

4.9.14 References.

4.10 This guide provides an overview of the unique characteristics influencing ebullition-facilitated NAPL/contaminant transport in aquatic sediment environments. This guide is not intended to provide specific guidance on sediment site investigation, risk assessment, monitoring, or remedial action.

4.10.1 This guide may be used by various parties involved in a sediment site, including regulatory agencies, project sponsors, environmental consultants, site remediation professionals, environmental contractors, analytical testing laboratories, data reviewers and users, and other stakeholders.

4.10.2 This guide does not replace the need for engaging competent persons to evaluate ebullition-facilitated NAPL/ contaminant transport in sediments. Activities necessary to develop a CSM should be conducted by persons familiar with NAPL/contaminant-impacted sediment site characterization techniques, physical and chemical properties of NAPL/ contaminants in sediments, fate and transport processes, remediation technologies, and sediment evaluation protocols. The users of this guide should consider assembling a team of experienced project professionals with appropriate expertise to scope, plan, and execute appropriate data acquisition activities.

5. Fundamentals and Considerations During Development of a Conceptual Site Model

5.1 Biogenic gases are generated in porewater as the result of microbial-facilitated degradation of OM. Ebullition-active sediment is typically rich in OM, which can originate from naturally occurring vegetation and organisms, as well as anthropogenic sources. The following sections provide an overview of gas ebullition and ebullition-facilitated transport of NAPL/contaminant processes, including factors that affect gas ebullition rates and NAPL/contaminant fluxes.

5.2 Biogenic gases are end products from the microbial degradation of OM, through various metabolic pathways that depend on availability of specific electron acceptors. The primary biogenic gases produced include CH₄, CO₂, and to a lesser extent N2 and H2S. Sulfate reduction and denitrification are energetically more favorable but produce lesser quantities of N_2 and H_2S . This is due to the limited availability of the external electron acceptors (NO₃⁻, SO₄²⁻) in sediments and presence of competing electron acceptors, such as oxygen, manganese, and iron. The energetics of biochemical reactions dictate that methane production can start only after the depletion of all other more energetically favorable terminal electron acceptors and under strictly anaerobic conditions. Methane production is observed beneath the zone of sulfate reduction in sediments. Methane concentrations in biogenic gases produced in sediments may range from 11 % to 79 %, depending on the predominant gas production pathway (1), (2), (3).³ Additional detail concerning the generation of biogenic gases in sediments is presented in Appendix X1

5.3 Factors affecting the rate of gas production (including how rates are affected) are summarized below and provided in more detail in Table 1. For methanogenesis to occur, microbial consortia capable of complete OM mineralization to CH4 and CO_2 are required to be present. These microbial consortia need sufficient labile OM (naturally occurring, anthropogenic, or both) and favorable geochemical conditions (anoxic redox conditions, electron acceptors present, favorable pH conditions). Additionally, sediment temperature influences the rate of microbial activity and gas generation; this changes seasonally and can be impacted by sediment depth, water depth, and groundwater (4). Relatively high sediment temperature affects gas production by stimulating the growth and activity of the microorganisms that degrade organic material and are responsible for gas production. Less gas is produced during colder conditions, when microbial activity decreases; whereas more gas is produced during warmer conditions, when microbial activity increases. Microorganisms responsible for gas production are metabolically active between 4 °C and 45 °C, with an optimal temperature range for methanogenesis between 35 °C and 42 °C (5).

5.4 Ebullition generally originates from shallower sediments, but methanogenesis occurs anywhere in the sediment column where conditions favor this process. The generation of methane in deeper sediment may not result in ebullition,

 $^{^{3}}$ The boldface numbers in parentheses refer to a list of references at the end of this standard.

Factor	Environmental Condition	Effect	Effect on Ebullition Rate	References
Factors Affecting the F	Factors Affecting the Rate of Microbial Activity	5.1		
Microbial consortia	Microbes (for OM mineralization to methane and carbon diovide)	Microbial activity	This is a baseline requirement ^{A} for gas production.	(11), (12), (13)
Labile OM	Total organic carbon Total organic carbon (naturally occurring, anthropogenic inputs, or both)	Microbial activity	Greater labile OM content increases rate.	(4), (6), (14)
Geochemical conditions		Microbial activity	This is a baseline requirement ⁴ for gas production. Affects the stability of microbiologic processes and the composition of gas generated.	(1), (2)
Sediment temperature	 Seasonal changes Water depth (can be tidally influenced) Sediment depth Groundwater 	Microbial activity	Greater sediment temperatures (up to 42 °C) increase rates.	(3), (4), (5), (15)
Factors Affecting the h	Factors Affecting the Rate of Gas Bubble Nucleation, Growth, and Mi	n, Growth, and Migration	5	
Availability of nucleation sites	 Accretion sites (either trapped gas on the surface of solid particles or preformed stable bubbles) 		This is a baseline requirement ⁴ for gas nucleation	(1)
Porewater conditions	 Gas concentrations (including groundwater seepage) 	Gas bubble nucleation and growth	Concentrations at saturation increase rate, dilution decreases rates.	(1), (16), (17)
	 Salinity 	Gas bubble nucleation and growth	Elevated salinity increases rate.	(18)
	 Tensile strength 	Gas bubble growth and migration $<$	Lesser tensile strength increases rate.	(8)
	Grain size	Gas bubble growth and migration	Larger grain size increases rate.	(19), (20)
Sediment conditions	Porosity Duild doncity	Gas bubble growth and migration	Greater porosity increases rate.	(20)
	Cohesion	Gas bubble growth and mingration	Lesser pulk defisity intereases rate.	(20) (8) (19) (20)
	Heterogeneity	Gas bubble growth and migration	Greater heterogeneity increases rate.	(20)
	Water depth (can be)4	2	
Overburden pressure	 Waterway activity 	Gas bubble nucleation, growth, and migration	Lesser overburden pressure increases rate.	(8), (19), (21), (22)
Atmospheric pressure	Weather changes	Gas bubble nucleation, growth, and migration	Lesser atmospheric pressure increases rate.	(8)
Factors Affecting the F	Factors Affecting the Rate of Gas Ebullition-Facilitated NAPL/Contar	ted NAPL/Contaminant Flux		
NAPL/contaminants	Presence of NAPL/ contaminants in ebullition active zone	Gas ebuilition-facilitated NAPL/contaminant flux	This is a baseline requirement ⁴ for gas ebulition- facilitated NAPL/contaminant flux.	(1), (23)
Oil-particle aggregates	 Presence of OPAs in ebullition active zone 	Gas ebullition-facilitated NAPL/contaminant flux	This is a baseline requirement ⁴ for transport of OPAs.	(6)

5

€ ∰ E3300 – 21

due to factors that inhibit bubble nucleation, growth, or migration through the sediment into surface water. The conditions present at a specific site can increase or decrease the likelihood for ebullition to be present and include porewater properties, sediment properties, and the overall environmental setting. These conditions are summarized below and additional details are provided in Table 1. This table discusses effects for a single factor; combinations of factors can result in synergistic or antagonistic effects.

5.4.1 Porewater properties including gas concentrations, salinity, and redox chemistry can impact the rate of gas nucleation and growth, along with the chemical composition of gas generated, as further detailed in Table 1 (2), (6).

5.4.2 The ability of bubbles to nucleate, grow, and migrate through the sediment bed is impacted by sediment properties including tensile strength, cohesivity, porosity, bulk density, grain size, and heterogeneity. Ebullition can only occur when the tensile strength of the sediment is exceeded by the gas pressure (7). Elevated tensile strength limits the ability of gas bubbles to form and move upward in the sediment column. Sediment tensile strength increases with depth below the mudline due to compression by the weight of overlying sediment and overburden pressure from the water column. Gas migration in cohesive sediments is generally a result of elastic expansion and fracture, while in noncohesive sediments, gas may migrate via capillary invasion, elastic expansion and fracture, or sediment fluidization. In noncohesive sediments, preferential pathways (due to lowered tensile strength for short period of time) can be developed through the process of ebullition. Porosity, bulk density, sediment heterogeneity, and grain size also influence bubble nucleation, growth, and migration, as further detailed in Table 1.

5.4.3 Environmental conditions, such as changes in pressure exerted on the sediment bed and the presence of groundwater discharge, can impact the conditions needed for ebullition to occur. The overburden pressure due to water depth and atmospheric pressure directly impacts tensile strength, which can limit ebullition rates, as described in 5.4.2. There is a relative increase in resistance to sediment fracturing in tidal environments near the time of high tide (as compared to low tide), as well as during flooding or other water depth changes, due to increasing water depth and overburden pressure. Currents, vessel traffic, and surface water outflows can produce changes in pressure and periods of high shear stress during which the cohesive strength of the sediment bed is exceeded, thereby increasing ebullition rates (8). Atmospheric pressure also impacts tensile strength through weather conditions and storm events, by changing the atmospheric pressure exerted on the overlying water and sediment bed.

5.4.4 Additionally, the overburden and atmospheric pressure also impact dissolved gas solubility. Increasing water depth and associated pressure increases the solubility of methane and other dissolved gases in sediment porewater, thereby increasing the dissolved concentrations that will be present at the onset of bubble nucleation. Once the greater solubility limit is reached and the porewater is saturated with gas, bubbles may form. This pressure-dependent limitation on bubble formation increases with water depth and depth below the mudline, as overburden pressure increases.

5.4.5 Groundwater discharge into a water body may provide additional nutrients or contaminants that enhance or limit the potential for ebullition. Gas may nucleate as pressure in the groundwater decreases as groundwater rises in the sediment column. Groundwater discharge may also impact gas composition through the advective transport of dissolved gases, as well as impact ebullition rates due to changes in sediment temperature (5.3).

5.5 For gas ebullition-facilitated transport (or flux) of NAPL/contaminants from sediment to surface water to occur, it is necessary to have favorable conditions for gas bubble formation and growth, then have the gas bubbles overcome the combined tensile strength and pressures to fracture the sediment, and finally have the gas bubbles generated in (or below) a zone where the NAPL/contaminants can attach to the gas bubbles as the gas bubbles migrate upward through the sediment to the water column. Due to the hydrophobic characteristics of NAPL and other organic contaminants, they preferentially sorb to the hydrophobic bubble surface and are transported through the sediment column to the overlying surface water. NAPL that is attached to a gas bubble and is transported to the surface of the water often spreads when the gas bubble breaks at the water surface and forms a sheen blossom. Surface water sheens can subsequently break down by photodegradation, biodegradation, volatilization, and dissolution of sheen constituents into the surface water, with a portion of the NAPL potentially resettling onto the sediment bed. Sheens may also be transported away from the point of release by advective and dispersive transport processes.

5.5.1 Similarly, surface sediments or oil-particle aggregates (OPAs) previously deposited in the sediment bed can also be transported through the water column by gas bubbles. Particles from the sediment column can sorb onto gas bubbles during their migration and be transported into the watercolumn. OPAs form due to the aggregation of a suspended oil droplet and suspended particulate matter. When the solid particles adhere to the oil droplet, the aggregates become denser than water, causing them to sink within the water column and deposit, becoming part of the sediment bed. Following deposition, the OPAs may be resuspended by subsequent gas ebullition that entrains the OPAs (9).

5.6 The composition of the gas bubbles formed in the ebullition process can provide information on the source(s) of the material undergoing methanogenesis to create the gas bubbles. In particular, isotopic analysis of carbon-14 (¹⁴C) can provide useful information about the age of the carbon source. If the sole carbon source is newer, more labile carbon (for example, plant detritus or sewage), the gas bubbles will contain detectable concentrations of ¹⁴C. If the sole carbon source is >50 000 years old (for example, petroleum or coal tar), the ¹⁴C concentrations in the gas bubbles will be non-detectable (10). In most systems, there will be a mix of newer and older carbon sources that will require interpretation. Further details on the application of ¹⁴C analysis in ebullition studies are presented in Appendix X2.

6. Initial Screening for Gas Ebullition and Ebullition Flux Measurement

6.1 Ebullition is a difficult process to quantify, due to its stochastic and episodic nature, as well as the differing scale of spatial and temporal variability in response to the combined effects of physical, chemical, and biological factors that influence gas ebullition (see Section 5). The interdependence of these factors and associated spatial and temporal variability make it difficult to develop a predictive gas ebullition model from field data.

6.2 Gas ebullition occurs ubiquitously in aquatic, tidal, and marine environments. However, for a remedial design to address ebullition, it is essential to establish that gas ebullition occurs with sufficient magnitude and prevalence that it may potentially impact remedy performance, or be an important contaminant transport pathway (or both of these). The main objectives of the assessment are to confirm the occurrence of gas ebullition, assess the intensity of ebullition events, ascertain the spatial extent of occurrence, and collect evidence of ebullition-facilitated transport of NAPL/contaminants to the water column (such as sediment resuspension or visual observations of sheens or NAPL on the water surface). The initial assessment is typically performed by conducting an ebullition survey using trained personnel. This may include observation of gas ebullition at the surface to estimate gas ebullition rates or underwater observation using cameras or divers.

6.3 Ebullition surveys are useful in establishing the occurrence of ebullition and delineating the ebullition active area to further refine the study area. Ebullition surveys are broadly classified as surface surveys or diver-based underwater surveys. Surface surveys include ebullition observations conducted using trained observers or the use of video cameras to remotely monitor ebullition events. During initial screening, surveys are typically conducted during periods when the greatest gas ebullition rates are expected to occur, to increase the probability of observing ebullition and ascertain the maximum spatial extent of its occurrence at a site. The timing of peak gas ebullition occurrence varies from site to site; influencing factors include seasonal sediment temperature changes, water level fluctuation, timing of low tides, and peak boat traffic in navigational channels. A preliminary understanding of the site is essential for planning ebullition surveys.

6.3.1 Ebullition surveys are usually conducted in a phased manner, starting with a larger study area that can cover the entire site or a significant portion of the site. Following initial observations, the study area extent is refined to include only areas with ebullition occurrence.

6.3.2 Surface Surveys:

6.3.2.1 Surface surveys can be conducted from the shoreline for well-defined or isolated gas seeps, or from a boat or kayak in the case of larger water bodies. For large sites (typically >0.5 acres), the survey area is divided into subareas of manageable size. Surveys conducted from a boat generally involve trained observers traversing the observation area for an extended duration to record the characteristics of an ebullition event. The duration of observations is subject to site conditions and may range from 1 h to 2 h, before and after low tides, an entire day (daylight hours), or during times of peak boat traffic. Ebullition surveys are typically conducted over multiple days; the data collection frequency can range from daily to weekly and may extend over multiple seasons or tidal cycles, depending on site conditions.

6.3.2.2 Video surveys can be useful to remotely monitor ebullition events and NAPL sheen. Video surveys are typically conducted using a stationary camera or an unmanned aerial vehicle (UAV). Stationary cameras are used to continuously monitor locations already known to exhibit ebullition or sheen blossoms (or both). Low wind conditions, cloud cover, and low sun angle provide the quiescent conditions and minimum glare needed to produce the best results using a stationary camera. UAV aerial surveys are typically employed for initial screening of a larger study area, during which the UAV is flown with a forward camera angle of 30°-45° for better downward visibility to observe the water surface and the surrounding areas. Aerial flyover surveys are more likely to observe NAPL sheens on the water surface than ebullition events and are useful in identifying larger ebullition active areas for additional monitoring. Like stationary cameras, UAVs can also be used for monitoring a specific location by hovering over the survey area for several minutes with the camera pointed downward. Hovering video surveys can be useful to record ebullition events and sheen blossoms in inaccessible areas.

6.3.2.3 Data collected from an ebullition survey may include the type of observation, which can be broadly categorized into gas bubble only, sheen blossom (that is, gas bubble with associated NAPL sheen), and NAPL sheen without observable gas bubble. Other supporting data from an ebullition survey may include rate of bubbling, bubble size, surface area extent of gas bubbling, quantity of the sheening observed at the surface, type of sheen, GPS coordinates, water depth, water temperature, sediment temperature, weather conditions, and boat traffic (if any). The GPS coordinates of all observations must be recorded. This information is useful in understanding the environmental conditions contributing to ebullition-facilitated NAPL/contaminant transport at a site. Care should be taken to not disturb the sediment during data collection. Multiple passes are recommended to improve the confidence of the observation.

6.3.3 Diver Surveys:

6.3.3.1 Diver surveys are also performed in multiple stages, but adequate underwater visibility is required to perform them. A broad area survey is usually conducted first to identify specific areas of interest that can be studied more thoroughly in a detailed survey (second stage). Broad area survey involves establishing a grid with transect line markers and weights set on the bottom of the water body. A diver swims the grid for 2 h -3 h to identify the location of gas bubbles. The diver is equipped with a camera, and the live footage is transmitted to a boat where observations are recorded. The diver can be equipped with a GPS unit to record the location of gas releases. Locations for the detailed survey are chosen based on results from the broad area survey. The selected locations are monitored periodically by a diver equipped with camera to record visual observations of gas release from the sediment.