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Standard Guide for Estimating Natural Attenuation Rates for Non-Aqueous Phase Liquids in the Subsurface[1]

This standard is issued under the fixed designation E3361; 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 is a guide for determining the appropriate method or combination of methods for the estimation of natural attenuation or depletion rates at sites with non-aqueous phase liquid (NAPL) contamination in the subsurface. This guide builds on a number of existing guidance documents worldwide and incorporates the advances in methods for estimating the natural attenuation rates.

1.2 The guide is focused on hydrocarbon chemicals of concern (COCs) that include petroleum hydrocarbons derived from crude oil (for example, motor fuels, jet oils, lubricants, petroleum solvents, and used oils) and other hydrocarbon NAPLs (for example, creosote and coal tars). While much of what is discussed may be relevant to other organic chemicals, the applicability of the standard to other NAPLs, like chlorinated solvents or polychlorinated biphenyls (PCBs), is not included in this guide.

1.3 This guide is intended to evaluate the role of NAPL natural attenuation towards reaching the remedial objectives and/or performance goals at a specific site; and the selection of an appropriate remedy, including remediation through monitoring of natural or enhanced attenuation, or the remedy transition to natural mechanisms. While the evaluation can support some aspects of site characterization, the development of the conceptual site model and risk assessment, it is not intended to replace risk assessment and mitigation, such as addressing potential impact to human health or environment, or need for source control.

1.4 Estimation of NAPL natural attenuation rates in the subsurface relies on indirect measurements of environmental indicators and their variation in time and space. Available methods described in this standard are based on evaluation of biogeochemical reactions and physical transport processes combined with data analysis to infer and quantify the natural attenuation rates for NAPL present in the vadose and/or saturated zones.

1.5 The rate estimates can be used for developing metrics in the corrective action decision framework, complementing the LNAPL Conceptual Site Model (LCSM) (Guide E2531).

1.6 The emphasis in this guide is on the selection and application of methods for quantifying rates of NAPL depletion or attenuation. It is assumed that the remediation endpoint has been defined for the site based on the remedial objectives to address composition or saturation concerns as defined in ITRC (2018) (**1**).[2] While the rates can be used to estimate the timeframe to reach the remediation endpoint under natural conditions, methods for estimating the total NAPL mass and timeframe are beyond the scope of this standard.

1.7 The users of this guide should be aware of the appropriate regulatory requirements that apply to 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.

1.8 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 sites with NAPL in the subsurface. The guide supplements characterization and remedial efforts performed under international, federal, state, and local environmental programs, but it does not replace regulatory agency requirements.

1.9 SI units are primarily used in the standard, however, units more commonly used in the industry are also represented.

1.10 The guide is organized as follows:

1.10.1 Section 2 lists referenced documents.

1.10.2 Section 3 defines terminology used in this guide.

1.10.3 Section 4 describes the significance and use of this guide.

1.10.4 Section 5 provides the conceptual model of natural attenuation processes and pathways.

1.10.5 Section 6 provides an overview and description of methods for the estimation of natural attenuation rates, including:

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

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1.10.5.1 Description of methods and available technologies:
(1) CO_2 efflux method
(2) Temperature gradient method
(3) Soil gas gradient method
(4) Groundwater monitoring method
(5) NAPL composition method

1.10.5.2 Screening or feasibility assessment of the method for the site conditions;

1.10.5.3 Background sources and correction methods;

1.10.5.4 Data interpretation, key considerations and challenges (for example, measurement frequency and locations and spatial/temporal averaging);

1.10.5.5 Applicability of methods for evaluating the performance of enhanced natural attenuation (bioremediation) systems;

1.10.5.6 Other method applications (for example, source delineation or estimating mass discharge rates).

1.10.6 Section 7 provides guidance on selection of a method or combination of methods applicable to site-specific conditions.

1.10.7 Section 8 provides example applications through case studies.

1.10.8 Section 9 lists keywords relevant to this guide.

1.10.9 Appendix X1 describes details of the CO_2 Efflux Method.

1.10.10 Appendix X2 describes details of the Temperature Gradient Method.

1.10.11 Appendix X3 describes details of the Soil Gas Gradient Method.

1.10.12 Appendix X4 describes details of the Groundwater Monitoring Method.

1.10.13 Appendix X5 describes details of the NAPL Composition Method.

1.10.14 Appendix X6 provides details of case studies discussed in Section 8.

1.10.15 Appendix X7 provides example estimates of NAPL quantity.

1.11 *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.*

1.12 *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:*[3]

D3328 Test Methods for Comparison of Waterborne Petroleum Oils by Gas Chromatography

D4448 Guide for Sampling Ground-Water Monitoring Wells

D4700 Guide for Soil Sampling from the Vadose Zone

D6866 Test Methods for Determining the Biobased Content of Solid, Liquid, and Gaseous Samples Using Radiocarbon Analysis

D7648/D7648M Practice for Active Soil Gas Sampling for Direct Push or Manual-Driven Hand-Sampling Equipment

D7663/D7663M Practice for Active Soil Gas Sampling in the Vadose Zone for Vapor Intrusion Evaluations

E1943 Guide for Remediation of Ground Water by Natural Attenuation at Petroleum Release Sites

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

E2876 Guide for Integrating Sustainable Objectives into Cleanup

E2993 Guide for Evaluating Potential Hazard as a Result of Methane in the Vadose Zone

2.2 *API Documents:*[4]

API, 2010 BioVapor, A 1-D Vapor Intrusion Model with Oxygen-limited Aerobic Biodegradation

API, 2017 Quantification of Vapor Phase-related Natural Source Zone Depletion Processes. American Petroleum Institute. Publication No. 4784

API, 2018 Managing Risk at LNAPL Sites. Frequently Asked Questions, Second Edition, Soil and Groundwater Research Bulletin No. 18, May 2018, updated May 8, 2019

2.3 *US EPA Standards:*[5]

EPA Method 8015 (SW-846), 2003 Nonhalogenated Organics Using GC/FID, Washington, DC

EPA Method 8260 (SW-846), 2018 Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), Washington, DC

US EPA, 2015 Technical Guide for Addressing Petroleum Vapor Intrusion at Leaking Underground Storage Tank Sites.

US EPA, 2016 Petroleum vapor intrusion modeling assessment with PVIScreen. U.S. Environmental Protection Agency Office of Research and Development. US EPA Report# EPA/600/R-16/175, p. 34

US EPA, 2017 Documentation for EPA's Implementation of the Johnson and Ettinger Model to Evaluate Site Specific Vapor Intrusion into Buildings. Version 6.0, Revised September 2017

2.4 *USGS Document:*[6]

USGS, 2021 Dissolved Gas N_2/Ar Sample Collection Procedure

3. Terminology

3.1 *Definitions:*

[3] 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.

[4] Available from American Petroleum Institute (API), 200 Massachusetts Ave. NW, Suite 1100, Washington, DC 20001, http://www.api.org.

[5] Available from United States Environmental Protection Agency (EPA), William Jefferson Clinton Bldg., 1200 Pennsylvania Ave., NW, Washington, DC 20460, http://www.epa.gov.

[6] Available from U.S. Geological Survey (USGS), 12201 Sunrise Valley Drive Reston, VA 20192, https://www.usgs.gov.

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3.1.1 *CO_2 efflux method, n*—a method for quantifying the natural source zone depletion rate that relies on measurements of CO_2 released from NAPL biodegradation in the subsurface and transported through diffusion and advection to the ground surface.

3.1.1.1 *Discussion*—The upward flux or efflux of CO_2 measured at the ground surface above the NAPL footprint is an indicator of the NAPL source depletion and can be used to estimate the natural source zone depletion rate with appropriate correction for background sources of CO_2. The method is described in Section 6 and Appendix X1.

3.1.2 *engineered remedy, n*—also referred to in other guidance documents as active remediation, is generally considered to be more resource intensive in terms of cost, energy use and greenhouse gas (GHG) emissions (Guide E2876).

3.1.2.1 *Discussion*—There can be a transition to natural remedy following the operation of an engineered remedy. Natural Remedy is commonly contrasted with Engineered Remedy as the two end members in the spectrum of remediation systems as shown in Fig. 1.

3.1.3 *groundwater monitoring method, n*—a method for quantifying natural attenuation rates that relies on groundwater sampling and analyses.

3.1.3.1 *Discussion*—The method can be used to obtain estimates of the attenuation rates of either bulk NAPL or groundwater COCs depending on the data collection and interpretation. Groundwater concentrations of hydrocarbons and geochemical indicators of redox reactions and dissolved gases, as well as hydrogeological parameters are used in the estimation of mass loss rates. The method is based on mechanisms contributing to mass loss in the saturated zone such as hydrocarbon dissolution and flow; biodegradation; degassing, bubble formation and ebullition. The method is described in Section 6 and Appendix X4.

3.1.4 *monitored natural attenuation (MNA), n*—a natural remedy documented through site characterization and monitoring.

3.1.4.1 *Discussion*—MNA has historically been focused on the assessment of spatiotemporal trends in concentrations of COCs in groundwater. Various tools for the estimation of natural attenuation have been advanced that consider all relevant processes including dissolution, volatilization, and biodegradation in both the vadose zone and the saturated zone. Therefore, methods for natural source zone depletion (NSZD) rate estimates for the NAPL are becoming more widely used to evaluate the effectiveness of MNA, in addition to those that historically addressed the monitoring of groundwater only. Estimating the rate of natural attenuation processes in the vadose zone and the saturated zone can also be used to guide the transition from an engineered remedy to a natural remedy such as MNA.

3.1.5 *NAPL composition method, n*—a method for assessing natural source zone depletion based on monitoring and data analysis of changes in NAPL composition over time.

3.1.5.1 *Discussion*—The natural attenuation processes such as dissolution, chemical and biological degradation, and volatilization all contribute to the NAPL weathering and hence a quantifiable change in the mass fractions of NAPL constituents. The method relies on assessment of the relative depletion of COCs or bulk NAPL as compared to marker constituents that are less susceptible to weathering. The method is described in Section 6 and Appendix X5.

3.1.6 *natural attenuation, n*—the naturally occurring mass loss of hydrocarbons in various phases and media (NAPL, vapor, soil, and groundwater) within a volume of soil or groundwater contamination.

3.1.6.1 *Discussion*—Natural attenuation occurs in and outside of the source zone where NAPL is present.

3.1.7 *natural remedy, n*—also referred to in other guidance documents as passive or knowledge-driven remediation, is generally a less resource intensive remediation system mainly relying on natural or in-situ and enhanced bioremediation measures.

3.1.7.1 *Discussion*—They are generally considered to have a lower cost, and environmental footprint in terms of energy consumption and GHG emissions (Guide E2876). Natural remedies may be selected as the only remediation measure at a site with minimal engineered intervention such as institutional controls. More typically, however, there is a transition to natural remedy after an engineered remedy has been in operation. MNA is an example of a natural remedy. Natural Remedy is commonly contrasted with Engineered Remedy as the two end members in the spectrum of remediation systems as shown in Fig. 1.

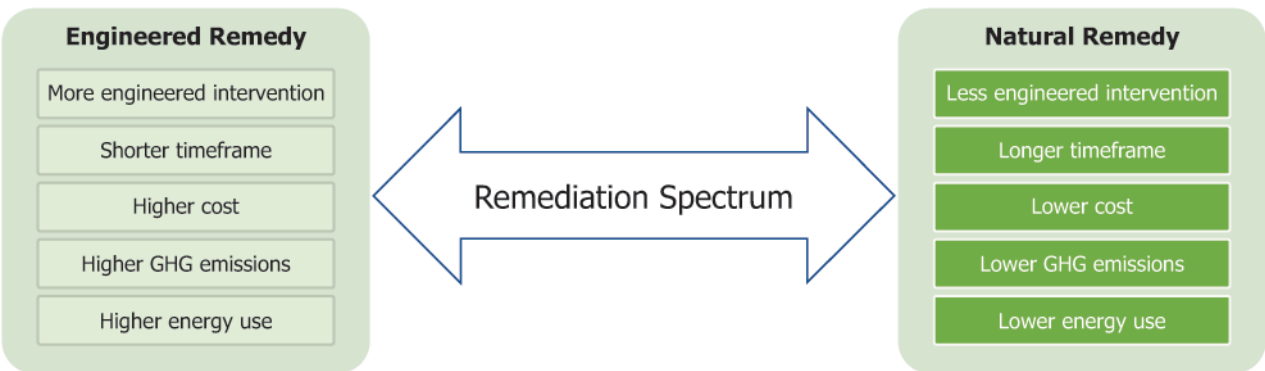

FIG. 1 Natural and Engineered Remedies Defined in Relative Terms as End-Members Across a Spectrum of Attributes for Remediation Systems

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3.1.8 *natural source zone depletion (NSZD), n*—the naturally occurring mass loss of hydrocarbons in NAPL source zones as a result of dissolution, volatilization, and biodegradation.

3.1.8.1 *Discussion*—NSZD is a subset of natural attenuation largely focused on the depletion of bulk hydrocarbons from a NAPL source present in the subsurface. NSZD rates can also be estimated for individual hydrocarbons depending on the selected method. The biogeochemical reactions and transport processes in the vadose zone and the saturation zone are shown in Fig. 2. These include dissolution and flow in the groundwater and biodegradation; dissolution into the porewater, volatilization and biodegradation in the vadose zone; and transport of gases across the capillary fringe. NSZD results in changes in the composition of the NAPL over time, which can impact NAPL forensics, and the risks associated with the NAPL such as in vapor intrusion, NAPL migration, and groundwater plume extent and stability.

3.1.9 *soil gas gradient method, n*—a method for quantifying the NSZD rate based on measurements of changes in soil gas composition with depth (vertical gradient) in the vadose zone resulting from biodegradation and transport of terminal electron acceptors (TEAs) and reaction byproducts (mainly O_2, CO_2, hydrocarbons, and CH_4).

3.1.9.1 *Discussion*—The most common application of this method is based on aerobic biodegradation of hydrocarbons in the vadose zone with diffusive oxygen transport from the ground surface. There are also variations on this approach for calculating COC-specific attenuation rate. The method is described in Section 6 and Appendix X3.

3.1.10 *temperature gradient method, n*—a method for quantifying the NSZD rate based on measurements of temperature and estimates of heat flux resulting from aerobic biodegradation of the NAPL and byproducts (methane) in the subsurface.

3.1.10.1 *Discussion*—The heat released is proportional to the rate of biodegradation and amount of hydrocarbon degraded, and results in thermal conduction and increase in in-situ soil temperature. Vertical profiles of soil temperature are used to infer the NAPL attenuation through biodegradation. The method requires correction for background sources of heat including heat exchange with the atmosphere at the ground surface. The method is described in Section 6 and Appendix X2.

4. Significance and Use

4.1 Guidance on management of NAPL sites and a large body of research effort contributing to their development (for example, ITRC 2018 (**1**); CRC CARE 2018 (**2**); CL:AIRE 2019 (**3**) and CRC CARE 2020 (**4**)) point to the significance of natural attenuation and NSZD in the evolution of NAPL source and the resulting distributions of COCs in soil, groundwater and vapor.

4.2 Examples of reported ranges in estimated natural attenuation rates are 300 – 7700 gallons of NAPL/acre/year (Garg et al. 2017 (**5**)); and 0.4 – 280 metric tons of NAPL/year (CRC CARE 2020 (**4**)).

4.3 The intent of this guide is to provide a standardized approach for the estimation of natural attenuation rates for NAPL in the subsurface. The rates can be used for establishing a baseline metric for those involved in the remedial decision-making process. There is a need for a systematic approach and refinement in data collection and interpretation for quantifying the spatially and temporally variable rates. Providing quality assurance in estimation of this metric will enable the assessment of relatively more engineered remedies as compared to natural remedies or MNA (Fig. 1), as well as estimation of the remediation timeframe. This comparison, when performed through a standardized approach, can lead to actionable metrics for transition to sustainable remedies through well-defined and transparent criteria. In the context of a spectrum of remediation options in terms of engineered and natural remedies (Fig. 1),

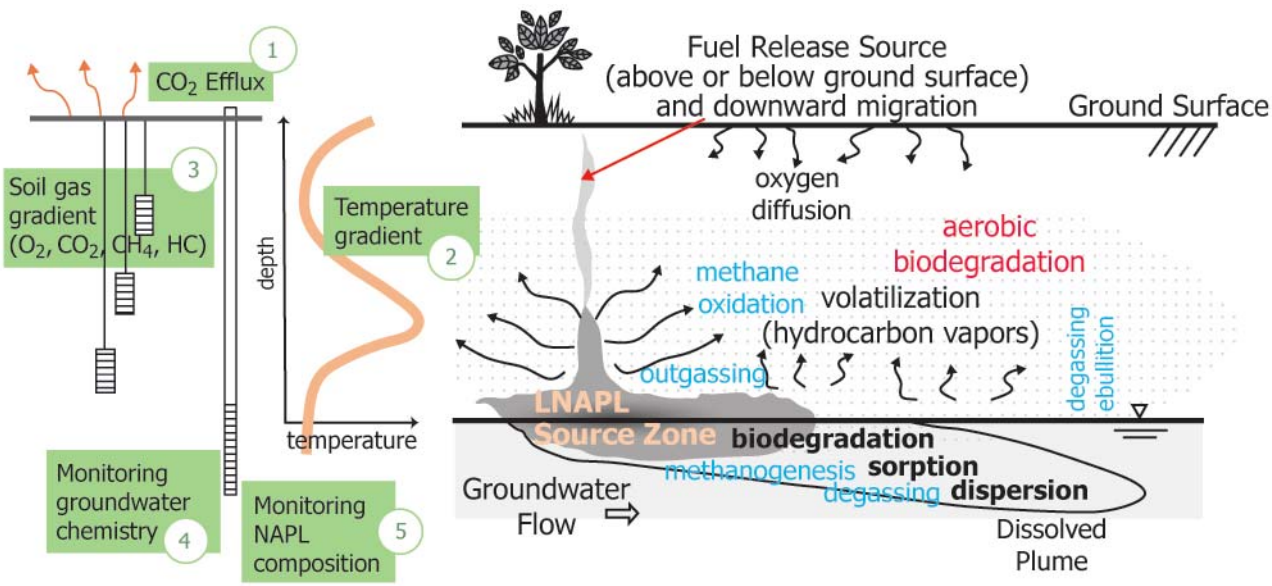

FIG. 2 Overview of Natural Attenuation and NSZD Processes, Methods, and Measurements

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the transition is from a relatively more engineered (or active remediation) to a relatively more nature-based remedy. When considered in the remedial decision-making process, estimates of natural attenuation rates can be used:

4.3.1 Before active remediation (as baseline to assess whether active remediation is needed);

4.3.2 During active remediation (as performance/optimization metric); and

4.3.3 At the end of active remediation (support transition to MNA or site closure).

4.4 Since natural attenuation results in changes to the NAPL composition over time, methods to estimate the natural attenuation rate also inform NAPL forensics, and the risks associated with the NAPL such as in vapor intrusion, NAPL migration, and groundwater plume extent and stability.

4.5 In addition, understanding of the magnitude of natural attenuation rates can contribute to addressing overarching questions in NAPL sites management, following initial characterization and risk assessment, such as:

4.5.1 What is the remediation timeframe under natural attenuation and how does it compare with the remedial timeframe of engineered remedies?

4.5.2 What are the current and future estimates of NAPL mass (or volume) remaining on site? The remaining mass can impact compositional concerns.

4.5.3 Under what scenarios (for example, size of release and/or presence of NAPL); and site conditions are the rates of NAPL natural attenuation significant in terms of reaching remedial objectives in accordance with regulatory criteria and remedial timeframe?

4.5.4 How do the rate estimates of natural attenuation change over time?

4.6 Common challenges encountered in the management of NAPL sites are:

4.6.1 Sites that remain under engineered (active) remediation over extended periods of time without reaching an acceptable endpoint.

4.6.2 Understanding what the long-term fate of NAPL bodies would be with and without engineered remedies.

4.6.3 Understanding the long-term fate of NAPL-related dissolved organic carbon (DOC) plumes.

4.6.4 Understanding NAPL movement and demonstrating stability.

4.7 A major obstacle in answering the questions in 4.5 and addressing the challenges in 4.6 is the availability of methods for estimation of reliable and quantifiable NAPL attenuation rates that can be implemented and reviewed by site managers, site owners and regulators. To address this challenge, the intent of this standard is to describe the available methods and their selection and application based on site conditions.

4.8 It is important to understand the applicability and use of the NAPL natural attenuation rates in decision making with regards to the requirement for an endpoint of an engineered remediation system. A merited transition from engineered to natural remedy, including MNA would result in a more sustainable approach to site management. MNA in the context of this standard includes the monitoring of natural attenuation rates in both the saturated zone and the vadose zone and complements previous standards (Guide E1943) focused on MNA in the saturated zone by inclusion of methods related to the vadose zone (Section 6).

4.9 The natural attenuation processes (Section 5) can impact remedial objectives in terms of addressing NAPL saturation (mobility or migration) or composition (COC concentrations in soil, groundwater or vapor), and therefore need to be included in the CSM. Natural attenuation, including NSZD, can reduce both NAPL saturation and constituent-specific mass.

4.10 Integration of natural attenuation rate estimate at the early stages of site management (that is, in the CSM) can result in its proper application to the remedial decision-making process, since natural attenuation can result in exposure risk reduction, as well as overall source mass reduction.

4.10.1 In most cases, identifying the occurrence of natural attenuation at a site or measuring the rate at a site is not sufficient in itself to accomplish remedial goals and regulatory requirements.

4.10.2 This guide provides methods for identifying the occurrence of natural attenuation, measuring the rate of natural attenuation and demonstrating how this data can be used for achieving remedial goals and regulatory requirements.

4.11 The advantages of estimating natural attenuation rates at sites impacted by hydrocarbon-based NAPL including petroleum, coal tars, or creosote is evidenced by examples where one or multiple methods for the rate estimates have been applied.

4.12 US EPA and State regulations or guidance that highlight the significance of natural attenuation at NAPL sites include:

4.12.1 Role of natural attenuation and specifically biodegradation in the vadose zone is demonstrated through analysis of data sets to substantiate the applicability of screening distances for petroleum vapor intrusion (US EPA, 2015, ITRC, 2014 (**6**)).

4.12.2 Adoption of MNA as a means to ensure long-term containment and reduction of dissolved phase plumes (Guide E1943, WI-DNR 2014 (**7**), ITRC 2018 (**1**)).

4.12.3 Additional technical aspects of NSZD pertaining to forensic evidence and weathering patterns have previously been employed by environmental professionals, regulatory agencies and legal courts on site specific projects.

4.13 Comparison of the natural attenuation rates to the removal rates achieved through engineered remedies over time, if applicable, and defining a threshold for transition from more engineered to more natural remedies has the potential to improve remedial decisions as demonstrated through case studies presented in this standard guide. This includes termination of a relatively engineered remedy and reliance on MNA.

5. Conceptual Model of Natural Attenuation Processes and Pathways

5.1 The natural attenuation processes that affect the distribution and evolution of a NAPL source zone are largely

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defined by the LCSM (Guide E2531; Guide E1943; Garg et al. 2017 (5); ITRC 2018 (1); CL:AIRE 2019 (3); CRC CARE 2020 (4)).

5.2 An overview of natural attenuation processes including NSZD is provided in Fig. 3.

5.2.1 Natural attenuation processes begin at the onset of a NAPL release to the subsurface and involve both physical transport processes, as well as biological and chemical reactions.

5.2.2 Reduction of NAPL mass in the source zone can occur in the vadose zone as well as the saturated zone depending on the location of the source zone with respect to the water table.

5.2.3 Natural attenuation is defined here as a broader concept that includes processes occurring within and away from the NAPL source zone in the vapor and/or groundwater plume (Fig. 3). These processes include:

5.2.3.1 Biodegradation;

5.2.3.2 Degassing, bubble formation and ebullition in groundwater;

5.2.3.3 Volatilization and transport in soil gas in the vadose zone;

5.2.3.4 Dissolution and flow in groundwater;

5.2.3.5 Sorption;

5.2.3.6 Back diffusion; and

5.2.3.7 Outgassing from direct biodegradation of NAPL source without dissolution into the aqueous phase.

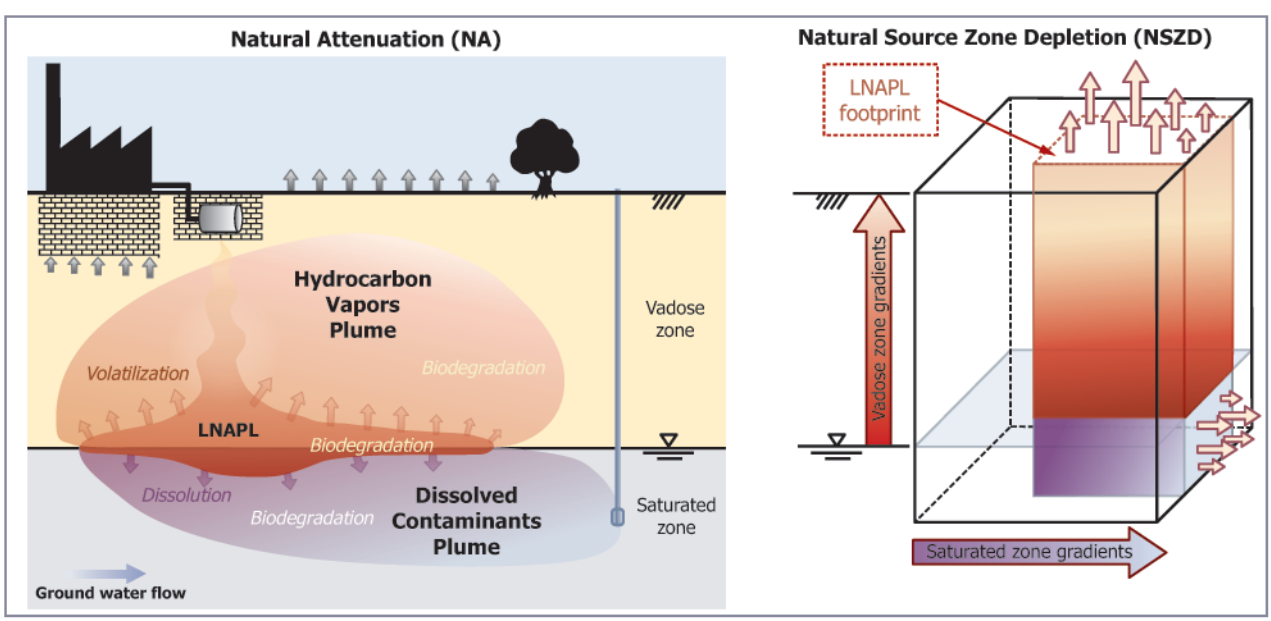
5.3 Historical representations of processes and pathways for natural attenuation of NAPL have focused on the saturated zone due to its impact on the extent and stability of groundwater plume of COCs (Guide E1943). Research studies on behavior of petroleum hydrocarbons in the vadose zone, particularly the significance of volatilization and aerobic biodegradation, driven in large part by the potential impact on vapor intrusion, have led to a greater emphasis on vadose zone processes.

5.4 Methods used to assess natural attenuation rates using soil gas profiles (for example, Lahvis and Baehr 1996 (8); Lahvis et al. 1999 (9); and Johnson et al. 2006 (10)), CO_2 flux at ground surface (for example, Sihota et al. 2011 (11); Sihota and Mayer 2012 (12); and McCoy et al. 2014 (13)) or temperature profiles (for example, Sweeney and Ririe 2014 (14)) above the NAPL source have indicated a greater range of natural attenuation rates than those estimated in the saturated zone (detailed review provided in Garg et al. 2017 (5)).

5.5 A number of guidance documents (for example, API 2017; ITRC 2018 (1); and CRC CARE 2018 (2) and 2020 (4)) have emerged in a relatively short span with research and publications improving the state of practice, particularly with respect to improved accuracy provided by new approaches to data analysis.

5.6 To the extent that risk drivers are the more volatile, soluble, and chemically or biologically degradable components of the NAPL source, estimates of bulk NAPL natural attenuation can be useful in remedial decision making and managing risk at sites (see Sections 4 and 6.4).

5.7 While most methods address the depletion of bulk NAPL (see 6.2 and 6.3), which ultimately reduce risks associated with both saturation and composition-based concerns, some methods can more directly address composition-based concerns by estimating the natural attenuation rate of COCs (notably one of the approaches presented for the soil gas



NOTE 1—The mass loss of petroleum hydrocarbons naturally occurring in any of the phases (NAPL, vapor, soil, and groundwater) within an area of soil or groundwater contamination. Natural attenuation occurs in and outside of the source zone where NAPL is present.

NOTE 2—The mass loss of petroleum hydrocarbons naturally occurring in NAPL source zones as a result of dissolution, volatilization, and biodegradation. NSZD is a subset of natural attenuation largely focused on the depletion of bulk petroleum hydrocarbons from a NAPL source present near the water table. NSZD rates can also be defined for individual hydrocarbons.

FIG. 3 Conceptual Representation of Natural Attenuation (Note 1) and Natural Source Zone Depletion (NSZD) (Note 2)

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gradient method in Appendix X3; and the compositional change method in Appendix X5).

5.8 Detailed descriptions of available methods for estimating natural attenuation rates and key processes considered for each method are provided in Section 6.

6. Natural Attenuation Estimation Methods

6.1 As described in the conceptual model of natural attenuation of NAPL (Section 5), there are a complex set of physical, chemical, and biological processes that shape the distribution and longevity of the NAPL body and its chemical constituents, some of which may be identified as COCs at a given site.

6.2 In order to untangle the interplay of these processes and enable the practical estimation of natural attenuation rates using readily available, or easy to obtain environmental data, five generalized methods based on key processes, target media and transport pathways are presented and are illustrated in Fig. 2.

6.3 For the various methods, it is important to note that some approaches are directly related to mass loss of specific COCs from the NAPL body, while others (temperature, O_2, CO_2, CH_4) are used to estimate "bulk" NAPL depletion.

6.4 Bulk NAPL depletion refers to the depletion of an unknown set of NAPL constituents. The term "bulk" does not imply uniform rates of depletion of the NAPL constituents. These methods do not provide information on hydrocarbon-specific rate of attenuation.

6.5 The five methods are defined as: *(1)* CO_2 flux at ground surface; *(2)* Vertical temperature profiles; *(3)* Gradients in soil gas concentrations; *(4)* Gradients in dissolved phase concentrations (including degassing); and *(5)* Changes in NAPL composition. Fig. 2 and Table 1 provide a summary of the methods with detailed descriptions in Appendix X1 to Appendix X5.

6.6 An overview of methods is provided in this section while detailed descriptions for each of the five methods can be found in Appendix X1 to Appendix X5.

6.7 Description of method and available technologies: A wide range of technologies and data analysis approaches are available depending on the specific method. For details, refer to Appendix X1 to Appendix X5. In general terms, the methods are compared as follows:

6.7.1 The methods can be divided based on measurement location (that is, ground surface or below ground surface) of data used to infer the rates. Method 1 using CO_2 flux requires measurements at the ground surface and is the least invasive method to employ at a site. All other methods require subsurface installations for sampling and analysis of relevant parameters. It is noted that some (and in some cases all) required subsurface installations may already be in place as part of site characterization, for example, existing monitoring wells and soil gas probes.

6.7.2 The estimated natural attenuation rates represent depletion of bulk NAPL-only for all methods except Method 5 using NAPL composition. Variations on Method 3 using soil gas concentrations and Method 4 using groundwater concentrations can be used to derive COC specific attenuation rates as described in Appendix X3 and Appendix X4, respectively.

TABLE 1 Summary of the Five Methods for Estimating Natural Attenuation Rates

Method	Type of Attenuation Measured[A]	Location of Processes & Pathway	Measurement Location
1. CO_2 Efflux	Bulk NAPL	Vadose zone[B]	Ground surface
2. Temperature Gradient	Bulk NAPL	Vadose zone[B]	Vertical profile mostly in the vadose zone & straddling the capillary fringe above the source zone
3. Soil Gas Gradient	Bulk NAPL & COCs	Vadose zone[B]	Vertical profile in the vadose zone above the source zone
4. Groundwater Monitoring	Bulk NAPL & COCs	Saturated zone	Profile along the groundwater flow path up- and down-gradient from the source zone; includes monitoring of dissolved gases
5. NAPL Composition	COCs	NAPL Source zone	Source zone

[A] The depletion rate of bulk NAPL directly addresses saturation-based concern. While estimates of COC attenuation rates have a more direct impact on composition-based concern, both bulk depletion of NAPL and COC attenuation impact the extent and longevity of the COCs in soil vapor and groundwater.
[B] Includes the transport of methane and other hydrocarbons produced from the biodegradation of NAPL in the saturated zone; and methane oxidation at the aerobic/anaerobic interface.

6.7.3 All methods use data collected over a short-term (minutes to several days) to estimate the natural attenuation rates, except for Method 5 using NAPL composition. This Method uses long-term monitoring data (that is, years) to infer rates and can be used to estimate the fraction of NAPL remaining at any point in time during which monitoring data is available. All other methods may require repeat measurements and data analysis to account for seasonal variations, while some can also be configured for continuous monitoring (for example, CO_2 flux and temperature).

6.7.4 Methods 1 to 4 utilize a change in a proxy measurement over space, for example a concentration gradient determined during a single monitoring event. Method 5 using NAPL composition utilizes long-term monitoring at a single location. Spatial coverage of this Method for site-wide estimation requires evaluation at multiple locations. This also applies to variations of Method 4 based on long-term monitoring and trend analysis of concentrations or mass discharge.

6.8 Screening or feasibility assessment of the method based on site conditions:

6.8.1 All methods except for Method 5 on NAPL composition are primarily applicable to site conditions where biodegradation plays a significant role in the natural attenuation estimates. Therefore, it is important to conduct an evaluation of NAPL biodegradation. These are generally based on changes in the distribution of the reactants and products of biodegradation reactions in groundwater and soil vapor such as

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6.8.1.1 Change in redox conditions and concentrations of terminal electron acceptors in groundwater between upgradient and downgradient locations from the NAPL source;

6.8.1.2 Soil gas concentrations in samples collected from soil gas probes or headspace of monitoring wells (field or laboratory measurements):

(1) Lower oxygen concentrations relative to atmospheric;

(2) Elevated carbon dioxide and methane concentrations; and

(3) Laboratory measurement of N_2 and Ar that are depleted or enriched relative to atmospheric (related to methane generation and pressure-driven flow) (Guide E2993; Amos et al. 2005 (**15**); and Molins et al. 2010 (**16**)).

6.8.1.3 Screening of the subsurface temperature profile within the NAPL-impacted areas for relative increase in the zone of aerobic/anaerobic interface (see Appendix X2).

6.8.2 Methods based on measurements in the vadose zone and dependent on downward flux of O_2 can be affected by ground surface covers or soil layers with low gas permeability such as a high clay or high moisture content. Low gas permeability also impacts the upward flux of CO_2 or hydrocarbons in soil gas. These factors specifically impact the applicability of the CO_2 Efflux, the Temperature Gradient and the Soil Gas Gradient Methods.

6.8.3 Method specific factors are discussed in Appendix X1 to Appendix X5.

6.9 Background sources and correction methods:

6.9.1 Aerobic biodegradation of methane or other hydrocarbons originating from the NAPL source zone can have a significant contribution to the rates estimated using Methods 1 to 3. Soil respiration, or aerobic biodegradation of natural soil organics, can confound the signature of measurement proxies for estimating the NAPL attenuation rate. There are generally two approaches for distinguishing between natural soil respiration (NSR) and respiration attributable to hydrocarbon or contaminant soil respiration (CSR).

6.9.1.1 One approach for determining the CSR portion of the attenuation rate is based on subtracting the contribution of NSR based on data obtained from an unimpacted area of the site (background location) from the data obtained from the NAPL footprint. Key considerations are the similarities between the subsurface soil and ground surface conditions between the NAPL area and the background location.

6.9.1.2 The alternative approach is the use of radiocarbon (^{14}C) analysis to correct for the portion of a rate attributable to CSR. This approach has been well demonstrated for Method 1 based on the assumption that CO_2 derived from fossil fuel is ^{14}C depleted, while CO_2 derived from modern organics is ^{14}C rich.

6.9.1.3 Key factors are the presence of soil layers rich in organics such as peat, vegetation and seasonal variability.

6.9.2 Further details on the application of the two approaches are discussed in Appendix X1 to Appendix X3.

6.10 Data interpretation and key considerations and challenges:

6.10.1 Considerations for data analysis and interpretation of estimated attenuation rates are highly dependent on the specific method, in addition to site-specific conditions. A solid understanding of the LCSM and the conceptual model of natural attenuation processes and pathways (Section 5) is essential for all methods.

6.10.2 The factors detailed for each method in Appendix X1 to Appendix X5 generally relate to subsurface and ground surface conditions. Method 1 using CO_2 flux is particularly sensitive to ground surface conditions; whereas Method 2 using temperature profiles and Method 3 using soil gas gradient are indirectly affected by these conditions in terms of O_2 availability and its effect on aerobic biodegradation; Method 4 using groundwater gradient and Method 5 using NAPL composition are not affected.

6.10.3 Spatial variability in subsurface and ground surface conditions is expected to result in variability in the estimated rates across the NAPL footprint. For this reason, all methods generally require measurements at multiple locations and a form of weighted spatial averaging or integration.

6.10.4 Considerations affecting measurement frequency and temporal variability are changes in groundwater elevation and seasonal variations in temperature and precipitation along with resulting changes in soil moisture content in the vadose zone. Temporal variability is expected to have the greatest impact on vadose zone Methods 1 to 3, and least impact on methods based on long-term monitoring data such as Method 5 based on NAPL composition.

6.10.5 Method specific recommendations for addressing spatial and temporal variability are provided in Appendix X1 to Appendix X5.

6.11 Applicability of the method for evaluating the performance of enhanced attenuation (bioremediation) systems.

6.11.1 Biodegradation forms the basis or the major component of Methods 1 to 4. The specific technology used in each method may be affected by the operation of a bioremediation system. For example, changes in temperature, soil gas and CO_2 flux data can be used for rebound testing of a soil vapor extraction (SVE) system.

6.11.2 Further details are provided in Appendix X1 to Appendix X5.

6.12 Other method applications:

6.12.1 Data obtained for site investigation and LCSM development can be used to assess the applicability of methods for estimating natural attenuation rates. Likewise, data obtained for Methods 1 to 5 can be used to inform the LCSM and remedial decision making. Examples include:

6.12.1.1 Some specific technologies for CO_2 flux measurements can be used for NAPL source delineation.

6.12.1.2 Data obtained for Method 4 on groundwater monitoring can be used to estimate dissolved mass discharge rates.

6.12.2 Method specific suggestions are provided in Appendix X1 to Appendix X5.

7. Decision Process for Appropriate Selection of Method and Application

7.1 This section is intended to provide guidance on selection of a method or combination of methods for estimating natural attenuation rates at sites with NAPL in the subsurface with the following considerations:

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7.1.1 Site conditions are unique and in addition to technical challenges, the logistics of implementation and availability of resources factor into the method selection, for example, access to available technology, instruments, or laboratory services; knowledge and expertise for data interpretation; and computational resources.

7.1.2 Ultimately, the application of any of the five methods presented can be used for decision-making towards sustainable remediation and risk reduction.

7.2 Applicability of each method depends on the underlying assumptions in the context of site conditions (Table 2).

7.3 Multiple lines of evidence approach through comparison of rates derived from different methods may increase level of confidence in estimates.

8. Example Problems

8.1 There are several techniques available for estimating the natural attenuation rates depending on site conditions, available resources and remedial concerns. These techniques are categorized into five general methods as described in Table 1 of this standard guide and described in detail in Appendix X1 to Appendix X5. This section provides practical, step-wise recommendations for example implementation of these methods, in addition to seven case studies of site-specific applications.

8.1.1 Example implementations for each of the five methods are provided in Figs. 4-8, noting that there are other variations in technologies and approaches than these examples. These examples and alternative approaches are covered in the respective Appendix X1 to Appendix X5.

8.1.2 Fig. 4 shows an example of the CO_2 Efflux Method using the dynamic closed chamber (DCC) for CO_2 efflux measurements. This is one of the various technologies described in Appendix X1.

8.1.3 Fig. 5 shows an example approach for estimating the natural attenuation rate from temperature monitoring data. This is one of the various approaches described in Appendix X2.

8.1.4 Fig. 6 shows an example approach for estimating the natural attenuation rate of bulk NAPL using soil gas monitoring data. This is one of the various approaches described in Appendix X3, which also includes approaches for estimating natural attenuation rates of specific COCs.

8.1.5 Fig. 7 shows an example approach for estimating the natural attenuation rates of bulk NAPL in the saturated zone, particular to sites that may have confined NAPL conditions. Additional information and considerations are provided in Appendix X4.

8.1.6 Fig. 8 shows the implementation and equations for estimating the natural attenuation rates based on the NAPL Composition Method. Additional details are provided in Appendix X5.

8.2 The case studies are described in Appendix X6 in terms of the following site conditions:

8.2.1 Site location and climate;

8.2.2 NAPL Type;

8.2.3 Lateral and vertical extent of the NAPL source zone (for example, with respect to the water level and the groundwater flow direction);

TABLE 2 Summary of the Method Assumptions And Site-Specific Considerations[A]

Method	Underlying Assumptions	Site Conditions
CO_2 Efflux	• Attenuation of NAPL constituents through biodegradation • Complete mineralization of NAPL constituents to CO_2 • CO_2 transport in soil gas from the source to the ground surface (point of measurement) • Background source: CO_2 produced from natural soil respiration • Estimate the portion of CO_2 efflux attributable to contaminant biodegradation	• Ground surface cover[B] • Vegetation • High natural organics (for example, peat) • High permeability soils and barometric pumping • Low gas permeability soils • Preferential pathways (for example, utilities)
Temperature Gradient	• Attenuation of NAPL constituents through aerobic biodegradation and oxygen availability • Production of biogenic heat from aerobic oxidation of hydrocarbons (notably methane) • Background correction for heat exchange with the atmosphere and other sources of heat in the subsurface	• Low gas permeability surface cover that could limit soil gas transport[B] • High natural organics (for example, peat) • Confined NAPL conditions (Guide E2856) • Geologic or anthropogenic sources of heat not related to the NAPL
Soil Gas Gradient	• Spatial changes in soil gas composition – vertical profile in the vadose zone resulting from biodegradation of NAPL constituents • Vertical gradients in O_2, CO_2, or hydrocarbon concentrations in soil gas • Diffusive gas transport in the vadose zone	• Low gas permeability surface cover that could limit O_2 ingress[B] • Low gas permeability soils • Soil gas advection from barometric pumping effects or high methane concentrations
Groundwater Monitoring	• Spatial (up-and down-gradient of the source) changes in the groundwater chemistry including dissolved gas concentrations resulting from biodegradation of NAPL constituents in the saturated zone • Dissolution and flow of NAPL constituents in groundwater	• Availability of groundwater monitoring data and hydrogeologic parameters • Assessment of confined NAPL conditions (Guide E2856) for data interpretation[C]
NAPL Composition	• Changes in the composition of NAPL constituents over time • NAPL sampled consecutively from a single location is representative of the same NAPL body over time (monitoring period)	• Finite NAPL mass with no additional releases during the assessment period • Availability of NAPL compositional data over time (minimum of approximately four years and 9 to 10 NAPL samples) • Conversion of fraction/percent rates into volumetric rates will require an estimate of total NAPL volume at the onset of the monitoring period

[A] Additional details available in Section 2 of respective appendix for each method.
[B] O_2 ingress and aerobic biodegradation is not inhibited at all paved sites as demonstrated, for example, by Smith et al. (2021) **(17)** at a former fuel retail site with concrete and asphalt pavement. The authors note presence of cracks in the pavement described as generally in poor state of repair. In addition, analysis of soil gas data from multiple sites by Roggemans et al. (2001) **(18)** with paved and uncovered ground surface did not reveal an obvious relationship between the site characteristics and aerobic biodegradation in the vadose zone.
[C] Confined NAPL conditions can lead to higher methane concentrations in the saturated zone, degassing and ebullition (Appendix X4).

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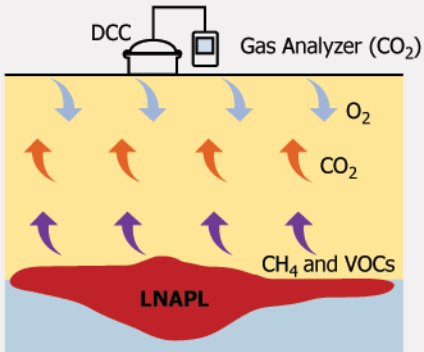
CO_2 Efflux Method



Method: upward flux of CO_2 measured with DCC at the ground surface above the LNAPL footprint is used to estimate the NSZD rate. DCC (Dynamic Closed Chambers) are open-bottom containers in which the vapors emitted from the subsurface are accumulated over time. The concentration increase in the chamber (dC/dt) is continuously measured with a gas analyzer (for example, IR sensor).

Step 1 – Install the DCC: Before the installation of the chambers, the portion of the soil area selected for the monitoring must be cleaned by any grass that could alter the emission of vapors from the subsurface.

Step 2 – Estimate the CO_2 flux: On the basis of the concentration increase in chamber (dC/dt) that is continuously measured with the gas analyzer, it is possible to estimate the total CO_2 flux (J_{CO2}), for example, by linear interpolation of the measured CO_2 concentration vs. time.

$$J_{CO_2} = \frac{dC}{dt} \cdot \frac{V}{A}$$

J_{CO2} = Total CO_2 flux (μmol $CO_2/m^2/s$)
dC/dt = CO_2 increase over time (μmol $CO_2/m^3/s$)
V = DCC volume (m^3)
A = DCC area (m^2)

Step 3 – Correct for background sources: The soil respiration contribution (J_{NSR}) must be determined and subtracted from the total CO_2 flux (J_{CO2}). This can be done by using radiocarbon (^{14}C) analysis; or by measuring the gas flux in a background location outside the LNAPL footprint with similar surface and subsurface conditions (see Appendix X1)

$$J_{CSR} = J_{CO_2} - J_{NSR}$$

J_{CSR} = attributed to NAPL soil respiration (μmol $CO_2/m^2/s$)
J_{CO2} = total measured (μmol $CO_2/m^2/s$)
J_{NSR} = attributed to natural soil respiration (μmol $CO_2/m^2/s$)

Step 4 – Estimate the NSZD flux, J_{NSZD}: convert the measured gas flux of CO_2 assuming a representative hydrocarbon (for example, octane):

$$J_{NSZD} = J_{CSR} \frac{M_w S_{HC:CO2} U}{\rho_o}$$

J_{NSZD} in gallons/acre/year.
M_w = Molar weight of hydrocarbon (g/mol)
$S_{HC:CO2}$ = Stoichiometric ratio of a mole of hydrocarbon degraded per mole of CO_2 produced
ρ_o = Density of hydrocarbon (kg/L)
U = Unit conversion factor = $33.7 \frac{s}{year} \times \frac{kg}{\mu g} \times \frac{m^2}{acre} \times \frac{gallon}{L}$

NOTE 1—Additional techniques and detailed method description are provided in Appendix X1.

FIG. 4 Example Implementation Steps for the CO_2 Efflux Method

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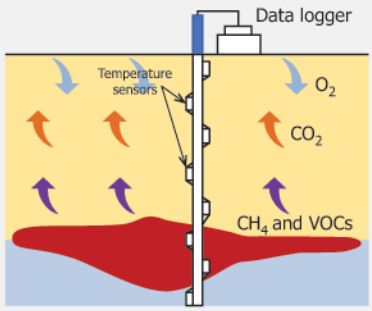
Temperature Gradient Method



Method: The temperature gradient method requires temperature data collected at discrete depths. Based on the temperature gradient in soil, it is possible to estimate the heat flux from biodegradation of NAPL that are converted to an estimate of NSZD rate. Various sensor technologies are available to determine the temperature profile in soil.

Step 1 – Identify the temperature profile: obtain the measured temperature profile, $T_m(x, t)$ at depth, x and time t at location of the NAPL source.

Step 2 – Correct for background sources: Select one of the three approaches (Appendix X2):

- Background correction (requires measurements at background location; estimate ΔT and follow Steps 3 to 5 below)
- Thermal correction from surface heating and cooling through temperature monitoring data ("single-stick" method: measurements at background location not required; Steps 3 to 5 do not apply; see Appendix X2)
- Thermal correction from surface heating and cooling through modelling (measurements at background location not required; estimate ΔT and follow Steps 3 to 5 below)

Step 3 – Approximate average daily $\Delta T(x)$ to the best fit polynomial through regression analysis:

- Regression forced through $\Delta T(0) = 0$
- Estimate the NSZD-related thermal gradients at the top and bottom that can be evaluated at time in seconds, t^i (on day i), adapted from Karimi Askarani et al. (2018)

$$T_m(x, t) = T_s(x, t) + \Delta T(x, t)$$

derivative of the polynomial function $\Delta T(x)$

$\left(\frac{d\Delta T}{dx}\Big|_{top}\right)$ at $x = 0$

$\left(\frac{d\Delta T}{dx}\Big|_{bottom}\right)$ at x = **depth** of the lower most temperature measurement below the water table

Step 4 – Calculate the energy balance based on the thermal gradients:
Taking into account thermal conduction both above and below the depth of peak temperature with heat transfer between the atmosphere and the groundwater, respectively. The energy balance equation yields:

$$\frac{dE_{sto}}{dt} = \dot{E}_{NSZD} - \dot{E}_{bottom} + \dot{E}_{top}$$

$$\dot{E}_{NSZD} = \frac{dE_{sto}}{dt} + \dot{E}_{bottom} - \dot{E}_{top}$$

rate of energy produced through biodegradation (W/m^2)

$\dot{E}_{top} = -\kappa_{unsat}\frac{d\Delta T}{dx}\Big|_{top}$ conductive energy flux at the top of the temperature profile (W/m^2)

$\dot{E}_{bottom} = -\kappa_{sat}\frac{d\Delta T}{dx}\Big|_{bottom}$ conductive energy flux at the the bottom of the temperature profile (W/m^2)

κ_{unsat} = unsaturated thermal conductivity (W/m/K)

κ_{sat} = saturated thermal conductivity (W/m/K)

Energy storage in units of J/m^2:

$$E_{sto} = C_{unsat}\int_0^{x_{wt}} \Delta T dx + C_{sat}\int_{x_{wt}}^{x_{bottom}} \Delta T dx$$

C_{unsat} and C_{sat} are the unsaturated and saturated heat capacity, respectively (J/m^3/K)

$$\frac{dE_{sto}}{dt} = \frac{E_{sto}|^{t^i} - E_{sto}|^{t^{i-1}}}{t^i - t^{i-1}}$$

Step 5 – Estimate the NAPL depletion flux, J_{NSZD}:
on volumetric basis (L m^{-2} s^{-1}):

$$J_{NSZD} = \frac{-\dot{E}_{NSZD}}{\Delta H(\rho/M_w)}$$

enthalpy ΔH (J/mol); density (g/L) and molecular weight (g/mol) of the representative hydrocarbon

NOTE 1—Additional techniques and detailed method description are provided in Appendix X2.

FIG. 5 Example Implementation Steps for the Temperature Gradient Method

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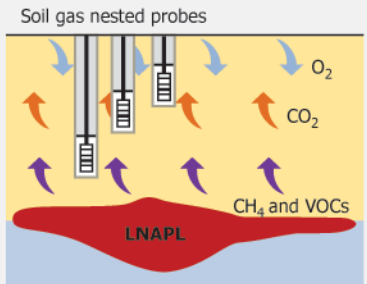
Soil Gas Gradient Method



Method: The soil gas gradient method requires soil gas concentration data collected at discrete depths in the vadose zone above NAPL. One approach is based on the gradients in O_2 and CO_2 concentrations in soil gas to estimate the O_2 and CO_2 fluxes resulting from hydrocarbon biodegradation. The O_2 and CO_2 concentrations in the soil gas can be determined with a portable gas analyzer.

Step 1 – Identify the profile: examine the soil-gas profiles to identify the behavior that best describes the field data (linear, semi-curvilinear or curvilinear profile).

Step 2 and Step 3 – Estimate the concentration gradient: Based on the selected behavior, estimate the concentration gradient (dC/dz) of O_2.

$$\begin{cases} \dfrac{dC(O_2)}{dz} = \dfrac{O_2(up) - O_2(low)}{\Delta z} & \text{(linear)} \\ \dfrac{dC(O_2)}{dz} = \dfrac{O_{2,z^*}}{LR_{O2}} & \text{(semi-curvilinear)} \\ \dfrac{dC(O_2)}{dz} = \dfrac{O_{2,max}}{LR_{O2}} & \text{(curvilinear)} \end{cases}$$

LR_{O2} = reaction length for oxygen (m)
$O_{2,max}$ = concentration at the surface (g/m^3)
O_{2,z^*} = concentration at depth z* at which the concentration profile (g/m^3) changes from linear to non-linear
O_2(up) and O_2(low) = concentrations in the upper and lower control points (g/m^3)
Δz = distance between the control points (m)

Estimate the reaction length for oxygen (Appendix X3)

$$LR_{O2} = \frac{\Delta z}{\ln[O_2(z)] - \ln[O_2(z+\Delta z)]}$$

$O_2(z)$, $O_2(z+\Delta z)$ = concentrations at z and z + Δz (g/m^3)
Δz = vertical distance between the sample points (m)

Step 4 — Estimate the diffusion coefficient: The diffusion coefficient (D^{eff}) for O_2 can be determined by site-specific measurements or using empirical equations.

Step 5 — Estimate the mass flux: can be estimated using Fick's law.

$$J_{O_2} = -D^{eff}\frac{dC}{dz}$$

J_{O2} = Total O_2 flux (g/m^2/s)
D^{eff} = Diffusion coefficent (m^2/s)
dC/dz = O_2 gradient (g/m^4)

Step 6 – Correct for background sources: correct the O_2 flux to account for natural soil respiration contribution (J_{NSR}) (radiocarbon analysis or background correction as shown below).

$$J_{CSR} = J_{O_2} - J_{NSR}$$

J_{CSR} = O_2 flux attributed to NAPL soil respiration (g/m^2/s)
J_{O2} = Total O_2 flux determined with the gradient method (g/m^2/s)

Step 7 – Estimate the NSZD flux, J_{NSZD}: convert the gas flux of O_2 assuming a representative hydrocarbon (for example, octane):

$$J_{NSZD} = J_{CSR}S_{HC:O2}$$

J_{NSZD} in gallons/acre/year
$S_{HC:O2}$ = Stoichiometric mass ratio of *g* of hydrocarbon degraded per *g* of O_2 consumed

NOTE 1—Additional techniques and detailed method description are provided in Appendix X3.

FIG. 6 Example Implementation Steps for the Soil Gas Gradient Method

8.2.4 Type of the ground surface cover (over the NAPL footprint);

8.2.5 Remedial concern(s) at the site, such as:

8.2.5.1 Remedial concern is composition-based, where concentrations in soil, groundwater or vapor exceed regulatory criteria;

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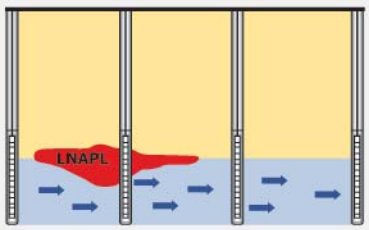
Groundwater Monitoring Method

Groundwater monitoring wells



Method: This method relies on the design of a groundwater sampling and analysis program for the estimation of natural attenuation rates. The example implementation takes into account the key processes in the saturated zone that result in mass loss from the NAPL source zone:
1) hydrocarbon dissolution and flow;
2) hydrocarbon biodegradation; and 3) degassing.

Step 1 – Estimate source mass depletion rate due to dissolution and flow:

$$R_{sat-dis} = q_d\, HW\, C_d$$

$R_{sat-dis}$ = source zone mass depletion rate due to dissolution (kg/day)

H = thickness of dissolved-phase constituent plume leaving the downgradient edge of the source zone (m)
W = width of dissolved-phase constituent plume leaving the downgradient edge of the source zone perpendicular to groundwater flow (m)

q_d = specific discharge of groundwater through the source zone ($\frac{m^3\ water}{m^2\ day}$)
C_d = area-averaged dissolved concentration at the downgradient edge of the source ($\frac{kg}{m^3\ water}$)

Step 2 – Estimate the assimilative capacity, A_C based on groundwater monitoring data:

$$A_C = \sum_{i=1}^{6} B_{C_i}$$

B_{C_i} = the biodegradation capacity of each biodegradation reaction, i

Biodegradation Reaction	Biodegradation Capacity	Geochemical Indicator
Aerobic respiration	B_{C_1}	O_2
Denitrification	B_{C_2}	NO_3^-
Iron (III) reduction	B_{C_3}	Fe^{2+}
Manganese (IV) reduction	B_{C_4}	Mn^{2+}
Sulfate reduction	B_{C_5}	SO_4^{2-}
Methanogenesis	B_{C_6}	CH_4

Example calculations of biodegradation capacities are available in Table X4-2.

Step 3 – Assess conditions for degassing:

- Conduct an assessment of confined NAPL/low permeability conditions (Guide E2856), where degassing can be a significant process.
- Collect groundwater samples for analysis of dissolved gases: CO_2, CH_4, N_2 and including O_2 and Ar, where practical, at multiple locations up-gradient, source zone and down-gradient of the NAPL source.
- Use the calculated partial pressures and the algorithm described in the Appendix of Amos et al. (2005) to calculate $\Delta[CH_4]$ to estimate the biodegradation capacity (B_{C_6}) attributed to methanogenesis in the saturated zone.

Step 4 – Estimate the rate of biodegradation in the saturated zone:

$$R_{sat-bio} = q_d\, HW\, A_C$$

This approach can be used at all sites, however, it is important to note that if there are measured natural attenuation rates from use of other methods in the vadose zone (CO_2 flux, temperature or soil gas gradient), these rates cannot be combined.

Step 5 – Estimate the total rate in the saturated zone, R_{sat} (kg/day):

$$R_{sat} = R_{sat-dis} + R_{sat-bio}$$

R_{sat} = total mass loss of hydrocarbons in the saturated source zone combination of dissolution and flow of the hydrocarbons ($R_{sat-dis}$) and the rate of hydrocarbons biodegraded ($R_{sat-bio}$).

NOTE 1—Additional techniques and detailed method description are provided in Appendix X4.

FIG. 7 Example Implementation Steps for the Groundwater Monitoring Method

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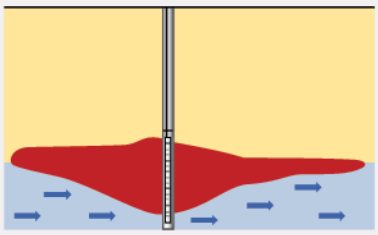
NAPL Composition Method

Groundwater/product monitoring well



Method: This method is based on monitoring and data analysis of changes in NAPL composition or mass fraction of constituents over time and requires long-term monitoring (a minimum of approximately four years). Quantitative depletion of the total NAPL mass is estimated from change in an identified conserved marker or sum of conserved markers in the NAPL over time.

Step 1. Identify the relevant constituents: based on the NAPL type and GC/FID data; these will represent the *N* constituents of NAPL for data analysis.

Step 2. Analyze data on mass fractions of NAPL constituents: χ_i (g-i/g-oil), i = 1 *to N* for each individual constituent i in the NAPL mixture identified in Step 1.

$$ln\left(\frac{\chi_{A,i}(t)}{1-\chi_{A,i}(t)}\right) = ln\left(\frac{\chi_{A,i}(0)}{1-\chi_{A,i}(0)}\right) - \kappa_{A,i}\,t$$

Use robust regression analysis method to estimate $\kappa_{A,i}$ (for example, Wilcox 2010) to increase the confidence in trend estimates for some data sets, over conventional regression methods.

- Assuming a binary mixture (A and B), each chemical, i is presumed to be a potential marker, A and the sum of the rest, B ($\chi_{B,i} = 1 - \chi_{A,i}$).
- The time evolution of mass fractions are assumed to follow an exponential curve with a relative rate, $\kappa_{A,i}$ as derived in DeVaull et al. (2020).

Step 3. Identify potential markers:
This step is based on ordered ranking (highest to lowest) of $\kappa_{A,i}$, where the constituents corresponding to the highest, rates are the most conserved constituents of the NAPL, and therefore indicate the best available near-conserved markers for the specific NAPL body under evaluation.

One viable method is to presume each constituent with a positive rate is a marker and estimate the final concentration and confidence limits (at the last measured time).

Step 4. Refinement on identifying potential markers:

This summation over multiple markers may tighten the confidence intervals on the estimated rates or estimated final concentrations.

The same procedure may be repeated for binary system of two mixtures: Mixture A represents the sum of q = 1 *to* i-th (ordered ranking of rates; top one, top two, top three, top four markers, etc.) and mixture B represents the sum of the remaining constituents. Analysis of fraction of total mass versus ordered summed constituents is used to select an optimum q.

Step 5. Estimate the effective rates:

Based on Equations 16 and 17 in DeVaull et al. (2020): at (t = 0) for total NAPL ($k_{eff,T}$ (t = 0); per year)

$$k_{eff,T}(t=0) = -\kappa_{A,q}\left(1-\chi_{A,q}(0)\right)$$

or individual constituents ($k_{eff,i}$ (t = 0); per year)

$$k_{eff,i}(t=0) = -\kappa_{A,q}\left(1-\chi_{A,q}(0)\right) + \kappa_{A,i}\left(1-\chi_{A,i}(0)\right)$$

or the half-life, $t_{half} = \frac{-\ln(0.5)}{\kappa_{eff}}$ (years).

Alternatively, the remaining fraction at the end of the monitoring time can be compared for individual constituents (fraction of initial remaining) based on Equation 13 in DeVaull et al. (2020):

$$\textit{Remaining fraction at time, } t = \frac{\chi_{A,q}(0) + (1-\chi_{A,q}(0))e^{-\kappa_{A,q}t}}{\chi_{A,i}(0) + (1-\chi_{A,i}(0))e^{-\kappa_{A,i}t}}$$

NOTE 1—Additional techniques and detailed method description are provided in Appendix X5.

FIG. 8 Example Implementation Steps for the NAPL Composition Method

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8.2.5.2 Remedial concern is saturation-based in terms of NAPL presence, mobility and/or migration; or

8.2.5.3 Other as noted.

8.2.6 Intended application of the estimated rates with respect to the remedial concerns at the sites (based on site characterization, including natural attenuation rate estimates);

8.2.7 Factors considered in the selection of method(s);

8.2.8 Applicability of the natural attenuation rate estimates in support of decisions, such as:

8.2.8.1 Remedy selection;

8.2.8.2 Remedy transition;

8.2.8.3 Improved CSM; or

8.2.8.4 Other as noted.

8.2.9 Method(s) employed;

8.2.10 Estimated rates;

8.2.11 Approach used to calculate the rates based on the measurements;

8.2.12 Background sources considered and correction methods, if applicable;

8.2.13 Spatial coverage with respect to the NAPL footprint, where applicable (for example, transects; number of locations); and

8.2.14 Assessment of seasonal variability (for example, number and/or frequency of measurements).

8.3 The reported rates, across the seven sites and various methods employed, range from 100 to 10,000 gallons/acre/year.

8.3.1 For most examples, the measured rates reported as volumetric or mass flux, varied with location in the NAPL footprint and over time. Professional judgement is required to derive an average or representative range of NSZD rates for a site.

8.3.2 The integrated flux over the NAPL footprint reported in units of mass or volume per unit time (for example, g/day or gallons/year) is typically used as a baseline metric for comparison to the performance of an engineered remedy. In this type of comparison, the NSZD rate reported in flux is integrated over the area marked by the radius of influence of the engineered remedy. This form of reporting and comparison is used to inform the remedy transition to natural mechanisms.

8.3.3 The reported rates in mass or volumetric flux (for example, g/m^2/day or gallons/acre/year) are typically used to evaluate the effectiveness of natural attenuation mechanisms, as well as the variations over time and the NAPL footprint.

8.4 Case study #5 demonstrates the use of the estimated natural attenuation rate of approximately 200 gallon/acre/year as a baseline metric to assess the performance of the engineered (active) remedy as compared to MNA.

8.5 The methods described in this standard can be used for estimating the rate of natural attenuation at a given time or data collection event. The rates can vary not only seasonally, but are expected to decrease over time as the more soluble, volatile and biodegradable constituents of the NAPL diminish. Therefore, an assumption of constant NSZD rate over time for estimating the timeframe for remediation under natural attenuation is not recommended. Davis et al. (2022) (**19**) reported NSZD rates spanning over two decades using the soil gas gradient method at a petroleum site with gasoline and diesel impacts. This study reported decreases in NSZD rate estimates by a factor of approximately 3 to 6 over a 14-year time period for diesel; and greater decrease by a factor of 9 to 27 over one decade for gasoline. In an earlier study at a crude oil spill site, Chaplin et al. (2002) (**20**) estimated hydrocarbon mass loss rates due to biodegradation in the vadose zone that decreased from approximately 11 kg/d to 2.0 kg/d over the span of 12 years. The rates were determined using the soil gas method with a reactive transport modeling approach and calibration to O_2, CO_2 and CH_4 concentration data in soil gas.

8.5.1 While estimates of timeframes for remediation under natural attenuation are beyond the scope of this guidance and challenging to estimate given the changing rates and site conditions over time, a qualitative assessment for sites at later stages of remediation with residual NAPL remaining in soil may be appropriate as illustrated in Appendix X7. The estimates of NAPL volume would be expected to be much greater for sites with NAPL saturations exceeding residual saturation. Example calculations of the specific volume of TPH in soil using the API LDRM software, range from approximately 25,000 gallons/acre for a 1-foot LNAPL thickness in well for silty sand soil, to 550,000 gallons/acre for a 5-ft LNAPL thickness in well for coarse sand. Compared to the estimates in Table X7.1 for residual TPH in soil at sites with weathered LNAPL, the estimates for sites with free product in wells are greater by approximately an order of magnitude. Accordingly, the estimates of timeframes for remediation would be greater by at least an order of magnitude.

8.5.2 There are other approaches available for calculating the NAPL volume with relatively higher accuracy (for example, within a factor of two) at any given time. Techniques for high resolution site characterization (HRSC) using, for example, Laser-Induced Fluorescence (LIF) data can be used alongside high density soil sampling for correlation with TPH concentrations in soil. However, these data can be costly to obtain at most sites and are not always available as part of the site characterization. Where they are available, the LIF data can be correlated with the TPH concentrations in soil (using 10 or more soil samples), and the total mass of hydrocarbon can be estimated based on a weighted spatial average using an interpolation algorithm and contouring software for the time that both data sets are collected. Correlation of LIF data with TPH concentrations in soil is only applicable to data collected concurrently (that is, soil sampling and LIF data collected during the same monitoring event). This is due to the changing composition of the NAPL over time (see Appendix X5) and the sensitivity of the HRSC data to specific constituents in the NAPL such as polycyclic aromatic hydrocarbons (PAHs). Therefore, time series LIF should not be used to calculate a difference in mass over time, as the changing NAPL composition between the two time points also alters the correlation between TPH concentrations in soil and LIF data. It is recommended to quantify and state the uncertainty associated with the use of this approach.

8.5.3 For sites at later stages of remediation and weathered and/or residual NAPL remaining, trend analyses of the attenuation of COC-specific concentrations may be more appropriate

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