

Quantification of Vapor Phase-related Natural Source Zone Depletion Processes

API PUBLICATION 4784
FIRST EDITION, MAY 2017



AMERICAN PETROLEUM INSTITUTE

Special Notes

API publications necessarily address problems of a general nature. With respect to particular circumstances, local, state, and federal laws and regulations should be reviewed.

Neither API nor any of API's employees, subcontractors, consultants, committees, or other assignees make any warranty or representation, either express or implied, with respect to the accuracy, completeness, or usefulness of the information contained herein, or assume any liability or responsibility for any use, or the results of such use, of any information or process disclosed in this publication. Neither API nor any of API's employees, subcontractors, consultants, or other assignees represent that use of this publication would not infringe upon privately owned rights.

API publications may be used by anyone desiring to do so. Every effort has been made by the Institute to ensure the accuracy and reliability of the data contained in them; however, the Institute makes no representation, warranty, or guarantee in connection with this publication and hereby expressly disclaims any liability or responsibility for loss or damage resulting from its use or for the violation of any authorities having jurisdiction with which this publication may conflict.

API publications are published to facilitate the broad availability of proven, sound engineering and operating practices. These publications are not intended to obviate the need for applying sound engineering judgment regarding when and where these publications should be utilized. The formulation and publication of API publications is not intended in any way to inhibit anyone from using any other practices.

Any manufacturer marking equipment or materials in conformance with the marking requirements of an API standard is solely responsible for complying with all the applicable requirements of that standard. API does not represent, warrant, or guarantee that such products do in fact conform to the applicable API standard.

All rights reserved. No part of this work may be reproduced, translated, stored in a retrieval system, or transmitted by any means, electronic, mechanical, photocopying, recording, or otherwise, without prior written permission from the publisher. Contact the Publisher, API Publishing Services, 1220 L Street, NW, Washington, DC 20005.

Copyright © 2017 American Petroleum Institute

Foreword

Nothing contained in any API publication is to be construed as granting any right, by implication or otherwise, for the manufacture, sale, or use of any method, apparatus, or product covered by letters patent. Neither should anything contained in the publication be construed as insuring anyone against liability for infringement of letters patent.

The verbal forms used to express the provisions in this document are as follows.

Shall: As used in a standard, “shall” denotes a minimum requirement in order to conform to the standard.

Should: As used in a standard, “should” denotes a recommendation or that which is advised but not required in order to conform to the standard.

May: As used in a standard, “may” denotes a course of action permissible within the limits of a standard.

Can: As used in a standard, “can” denotes a statement of possibility or capability.

Contents

	Page
1 Introduction	1
1.1 Background	1
1.2 Document Objectives	2
1.3 Intended Audience and Use	2
1.4 Guidance Applicability and Limitations	2
1.5 Document Content Reference Key	3
1.6 Data Uses for NSZD Measurements	3
1.7 Site Applicability and Technology Limitations	3
2 Theory of NSZD	6
2.1 Attenuation Processes	9
2.2 Thermal Signatures of Biodegradation	16
2.3 Estimation of Natural Source Zone Depletion	17
3 General NSZD Evaluation Considerations	17
3.1 Program Design Considerations	17
3.2 Gas Flux Monitoring Field Implementation	24
3.3 Data Evaluation	27
4 Gradient Method	30
4.1 Method Description	30
4.2 Program Design Considerations	31
4.3 Field Monitoring	36
4.4 Data Evaluation	40
5 Passive Flux Trap Method	41
5.1 Description	41
5.2 Program Design Considerations	41
5.3 Trap Deployment and Retrieval	43
5.4 Data Evaluation	45
6 Dynamic Closed Chamber Method	47
6.1 Description	47
6.2 Program Design Considerations	48
6.3 Survey Implementation	50
6.4 Data Evaluation	52
7 Emerging Methods	54
7.1 Biogenic Heat Monitoring	54
7.2 CH ₄ Flux Monitoring	58
7.3 ¹⁴ C Isotopic Correction for the Gradient and DCC Methods	59
8 Conclusions	60
8.1 Key Points of Guidance	60
8.2 Future Research Needs	61
Annex A (informative) Example Procedures	63
Annex B (informative) Case Study of Three NSZD Estimation Methods	91
Bibliography	110

Figures

1-1 Conceptualization of Vapor Phase-related NSZD Processes at a Petroleum Release Site	6
2-1 Conceptualization of Saturated Zone NSZD Processes	10

Contents

Page

2-2	Conceptualization of Vapor Phase-related NSZD Processes	12
2-3	Conceptualization of Vapor Phase-related NSZD Processes (a) with and (b) without Hydrocarbon Impacts in the Vadose Zone	15
3-1	Example Use of Nomograms to Estimate NSZD Rates	21
3-2	Example Placement of Survey Locations for DCC Method	25
3-3	Example Conceptual Depiction of Site-wide NSZD Rate Contouring	29
4-1	Schematic of Gradient Method Monitoring Setup with (a) and without (b) Hydrocarbon Impacts in the Vadose Zone	33
4-2	Conceptualization of Soil Gas Concentration Profiles with (a) and without (b) Hydrocarbon Impacts in the Vadose Zone	34
4-3	Choice of Measurement Points and Influence on Estimated Gradient CO ₂ Gradient in Soil with (a) and without (b) Hydrocarbon Impacts in the Vadose Zone	35
4-4	Determination of b Parameter in Equation 4.2 from Nonreactive Tracer Test Measurements of Mass and Vapor Recovery (Excerpt from Johnson et al. 1998)	38
5-1	Schematic (Left) and Photo (Right) of a Passive CO ₂ Flux Trap	42
6-1	LI-COR 8100A DCC Apparatus and Setup	48
6-2	Example Output from a CO ₂ Efflux Measurement Using a DCC	53
7-1	Schematic Diagram of NSZD-derived Heat Flux and a Subsurface Thermal Profile	56
B-1	Site Layout and Locations of NSZD Monitoring	92
B-2	Cross Section A-A'—Soil Texture, LNAPL Occurrence, and NSZD Monitoring Locations	93
B-3	Soil Gas Concentration Depth Profile at NSZD-1	97
B-4	Soil Gas Concentration Depth Profile at NSZD-2	97
B-5	Soil Gas Concentration Depth Profile at NSZD-3	98
B-6	Soil Gas Concentration Depth Profile at NSZD-4	98
B-7	Estimated Hydrocarbon Degradation Rate Using Depth and Porosity	100
B-8	Estimated Hydrocarbon Degradation Rate Using Effective Oxygen Diffusion Coefficient and Depth	101
B-9	Passive Flux Trap CO ₂ Efflux Measurement Results	105
B-10	DCC Results Compared with Soil Moisture and Ambient Temperature	107
B-11	Comparison of NSZD Rate Estimates	108

Tables

1	Summary of Intended Uses for This Guidance	2
2	Document Overview and Content Reference	4
2-1	Summary of Site Conditions that Preclude or Affect Vapor Phase-related NSZD Monitoring	7
3-1	Summary of Key LCSM Elements and Their Relations to NSZD	18
3-2	Spectrum of Data Use Objectives and the Associated Scope of NSZD Monitoring	19
3-3	NSZD Monitoring Method Screening Criteria	23
3-4	Units of NSZD Measurement	27
3-5	Example Representative Hydrocarbons and CO ₂ Flux Stoichiometric Conversion Factors	28
4-1	Sources of Uncertainty, Variability, and Mitigations Associated with the Gradient Method	37
5-1	Sources of Uncertainty, Variability, and Mitigations for the Passive Flux Trap Method	44
6-1	Sources of Uncertainty, Variability, and Mitigations Associated with the DCC Method	50
B-1	Summary of Key Content in the Case Study	91
B-2	Summary of Measurement Methods and Locations	92
B-3	Soil Gas Sampling Results	94
B-4	Oxygen Effective Diffusion Coefficients	100
B-5	Summary of Calculated NSZD Rates	103
B-6	Passive CO ₂ Trap Method Results	104
B-7	DCC Method Results	105

Acronyms and Abbreviations

°C	degrees Celsius
°F	degrees Fahrenheit
A/A	aerobic/anaerobic
AMS	accelerator mass spectrometry
ASTM	ASTM International
bgs	below ground surface
C ₇ H ₁₆	heptane
CH ₄	methane
cm	centimeter
CO ₂	carbon dioxide
CSM	conceptual site model
D ^{eff} _v	diffusion coefficient
DCC	dynamic closed chamber
DTSC	California Department of Toxic Substances Control
EPA	U.S. Environmental Protection Agency
Fe ²⁺	dissolved iron
FID	flame ionization detector
g/ft ² /d	gallons per square feet per day
g/m ² /d	gallons per square meter per day
gal/ac/yr	gallons per acre per year
gal/yr	gallons per year
GIS	geographic information system
GRO	gasoline-range organics
H ₂	hydrogen
H ₂ O	water
IRGA	infrared CO ₂ gas analyzer
ITRC	Interstate Technology and Regulatory Council
lb/ac/d	pounds per acre per day
lb/d	pounds per day
lb/yr	pound per year
LCSM	LNAPL conceptual site model
LIF	induced fluorescence
LNAPL	light non-aqueous phase liquid
m	meters
mg/L	milligrams per liter
Mn ²⁺	manganese
N ₂	nitrogen
NO ₃	nitrate
NSZD	natural source zone depletion

O ₂	oxygen
SO ₄	sulfate
PID	photoionization detector
ppm	parts per million
ppmv	parts per million by volume
PVC	polyvinyl chloride
QA/QC	quality assurance/quality control
RPD	relative percent difference
Sch	Schedule
SF ₆	sulfur hexafluoride
SO ₄ ²⁻	sulfate
SVE	soil vapor extraction
SZNA	source zone natural attenuation
TB	trip blank
TPH	total petroleum hydrocarbons
USDOT	U.S. Department of Transportation
VOC	volatile organic compound

Quantification of Vapor Phase-related Natural Source Zone Depletion Processes

1 Introduction

Natural source zone depletion (NSZD) has emerged as an important concept within the realm of environmental remediation. NSZD is a term used to describe the collective, naturally occurring processes of dissolution, volatilization, and biodegradation that results in mass losses of light non-aqueous phase liquid (LNAPL) petroleum hydrocarbon constituents from the subsurface.

This document provides practical guidance on NSZD theory, application, measurement methods, and data interpretation. It is intended to be used by practitioners to help plan, design, and implement NSZD monitoring programs in support of petroleum hydrocarbon site remediation.

This section of the document provides an introduction to the origin of the NSZD term, motivation, objectives, intended audience, and uses. To set the context for subsequent discussions, it also provides a broad overview on how measurements of NSZD can be used for decision making at remediation sites impacted by petroleum hydrocarbons.

1.1 Background

In 2000, the National Research Council issued its report on natural attenuation that included detailed discussion of the petroleum hydrocarbon degradation processes (NRC 2000). Largely leveraging work by others (Wiedemeier et al. 1995), it established a formal mass budgeting process by which biotic processes could be measured to estimate the assimilative capacity, or biodegradation capacity, within the groundwater via intrinsic microbiological processes. It focused solely on estimating dissolved hydrocarbon constituent losses within the saturated zone based on changes in various geochemical parameters (i.e. dissolved oxygen, nitrate, sulfate, ferrous iron, and methane [CH₄]). Its methods required only traditional groundwater sampling and field and/or laboratory analyses. In a field study by Borden et al. (1995), it was observed, however, that groundwater advection of electron acceptors and biodegradation byproducts alone was insufficient to explain the observed increase in carbon dioxide (CO₂) in the groundwater. They postulated that the transfer of atmospheric oxygen (O₂) into the groundwater plume from the soil gas could account for the remaining carbon and close the mass balance.

In 2006, source zone natural attenuation (SZNA) was introduced (Lundegard and Johnson 2006). SZNA was defined as the collective mass losses from LNAPL source zones via dissolution in groundwater, dissolved electron acceptor delivery and biodegradation, volatilization of organic compounds (VOCs), and emission of vapor phase biodegradation byproducts. Understanding vapor phase mass losses was a significant advancement in remediation practice, and demonstrated that saturated zone methods missed a significant portion of the total losses in LNAPL source zones. The first method demonstrated for monitoring vapor phase SZNA processes was the gradient method. This method consists of measuring soil gas concentration profiles of O₂, CO₂, CH₄, and the effective soil gas diffusion coefficient ($D_{eff,v}$), and using Fick's first law as a basis to estimate the rate of losses via vadose zone volatilization and aerobic biodegradation. The gradient method requires soil gas sampling and field and/or laboratory analyses.

In 2009, the Interstate Technology and Regulatory Council (ITRC) introduced a new term, natural source zone depletion (NSZD), to describe the same set of subsurface processes as encompassed by SZNA (ITRC 2009a). It proposed a systematic process to qualitatively assess and quantitatively measure NSZD through evaluation of source zone dissolution to groundwater, biodegradation of dissolved source zone mass, source zone volatilization to the vadose zone, and biodegradation of volatilized source zone mass. In addition to describing the use of the gradient method, it also discussed use of LNAPL chemical compositional change determinations, bench testing, and modelling as optional bases for NSZD quantification.

Since 2009, significant advances have been made in the methods used to measure NSZD, particularly with the vapor phase portion of the assessment. In addition to the gradient method (see Section 4), two new methods including the passive flux trap (see Section 5) and dynamic closed chamber (DCC) (see Section 6) are discussed herein. They are

included because they are published in peer-reviewed literature, are well-developed and have established industry-accepted field and analytical procedures, are accepted by the regulatory community, and are in widespread onsite use for NSZD monitoring. Other emerging methods for NSZD monitoring, including thermal monitoring using biogenic heat, are discussed in Section 7 because they are currently considered in a developmental stage.

1.2 Document Objectives

This document provides a summary of the theory and provides guidance on the use of three established NSZD methods: gradient, passive flux trap, and DCC. Its main objective is to provide a basis for improved consistency in the application and implementation of NSZD monitoring efforts and evaluation of NSZD data. Using prior terms of practice, it provides additional guidance on collection of Group II Data as specified in Johnson et al. (2006) to estimate NSZD rates.

Specifically, this document presents the following materials:

- summary of key elements of the current literature related to the theory and application;
- practical, experience-based guidance on planning, design, and implementation;
- sample procedures, calculations, and demonstration through a case study.

1.3 Intended Audience and Use

This guidance was written for a broad audience, including regulatory agencies, practitioners, and academia. Table 1 presents a summary of expected uses for the document.

Table 1—Summary of Intended Uses for This Guidance

Intended Audience	Intended Guidance Uses
Regulators—environmental remediation regulation compliance reviewers and case workers	Reference for reviewing proposed actions, work plans, and monitoring reports Staff educational and training material
Practitioners—site owners, consultants, and technology providers	Reference for developing work plans and field procedures Data interpretation support Staff educational and training material
Academia—professors, students, researchers	Reference for guiding future research needs Guide for design of related research Student educational and training material

1.4 Guidance Applicability and Limitations

This guidance is generally applicable to a wide range of environmental remediation sites containing petroleum hydrocarbon impacts in the subsurface. Hydrocarbon impacts in the subsurface can exist as sorbed hydrocarbon, residual LNAPL, mobile LNAPL, and migrating LNAPL (ITRC 2009b). Its use is appropriate at sites that have a need for theoretical, qualitative, or quantitative understanding of vapor phase-related NSZD processes. This guidance discusses three methods currently being applied to measure NSZD as it is expressed in soil vapor. It excludes other NSZD monitoring methods such as direct measurement of changes in LNAPL chemical composition, bench testing, and modeling that are addressed elsewhere (ITRC 2009a). Because the vapor phase component of NSZD is considered a critical component of an LNAPL conceptual site model (LCSM), this guidance is applicable to most petroleum release sites where risk management and/or remediation is ongoing.

This document captures the state of the practice. Like many environmental remediation monitoring methodologies, this is an evolving field and the practical portions of the document are subject to change as new approaches evolve. As such, this document is useful as a guide to develop site-specific plans and evaluate data, but its materials must be placed into proper context by a project team that is well versed in site conditions and project data quality and data need objectives. The reader is also advised to consult current literature for more recent advances and method improvements.

It is also important to note that because the methods described herein are emerging, few environmental remediation regulatory agencies have formalized the consideration of NSZD for decision-making purposes. The authors believe that this guidance will facilitate technically sound application and consistency, and thereby allow for more widespread use of NSZD monitoring to help advance remediation sites through the regulatory process toward closure.

1.5 Document Content Reference Key

Table 2 summarizes the content of each section in this document. Consult it to more expeditiously find materials of interest.

1.6 Data Uses for NSZD Measurements

NSZD measurements can be used for a wide variety of purposes. These include, but are not limited to the following.

- Refining the LCSM with quantification of petroleum hydrocarbon loss rates.
- Delineating the LNAPL footprint using vapor phase indicators of biodegradation.
- Estimating the short- and long-term rates of naturally occurring source mass removal.
- Assessing LNAPL stability through mass balance of losses and measured LNAPL mobility (Mahler et al. 2012).
- Comparing mass removal rates from NSZD to other ongoing remedial actions.
- Supporting a cost/benefit analysis of remedial technologies and evaluating the value of additional remediation.
- Evaluating remedial progress via periodic measurements during an active remediation program.
- Comparing pre- and post-remediation site conditions and evaluating the effectiveness of installed remedies.
- Optimizing the location of further remedial operations.
- Determining an endpoint for active remediation.

After alignment to a particular general data use above, site-specific data objectives can be defined and an NSZD monitoring program designed and implemented, as discussed in Sections 3 through 6 of this guidance.

1.7 Site Applicability and Technology Limitations

Figure 1-1 presents a conceptualization of subsurface conditions with annotations for vapor phase-related biodegradation byproducts of NSZD at a typical petroleum release site. It depicts the site conditions under which NSZD monitoring is typically applied. LNAPL and sorbed-phase petroleum hydrocarbons are present in the subsurface, with the majority within and below the zone of water table fluctuation. Anaerobic biodegradation predominates within this hydrocarbon impacted zone and creates CH₄ and smaller amounts of CO₂. Hydrocarbon compounds are volatilizing and offgassing along with the CH₄ and CO₂ from methanogenesis into the vadose zone. Where these gaseous NSZD byproducts meet atmospheric O₂, oxidation occurs. The oxidation of both CH₄ and

Table 2—Document Overview and Content Reference

Section Number and Title	Discussion Topics and Content
Section 1—Introduction	—Purpose of the guidance and how it serves an industry need —Explanation of focus on the vapor phase component of NSZD —Importance of NSZD in an LCSM —Summary of the document contents —List of various uses for NSZD data —Limitations of the document and technology —Selection process for go/no-go to implement NSZD monitoring —Site-specific criteria that are or are not a good fit for NSZD monitoring and how to adapt to them
Section 2—Theory of NSZD	—Definition of NSZD terminology and its component processes —Description of dissolution and biodegradation in the saturated zone —Description of volatilization and biodegradation in the vadose zone —Focus on processes that generate gaseous byproducts and their fate in the subsurface —Graphical composite conceptualization of important NSZD processes —Introduction to the thermal signatures associated with NSZD
Section 3—General NSZD Evaluation Considerations	—Development of a baseline understanding of NSZD through review of the LCSM —Options for theoretical assessment of NSZD to establish a benchmark for field measurements, including nomograms —Typical data objectives for NSZD monitoring programs —Basis for selection of a method for site-specific NSZD evaluation including a method screening table —Background correction procedures used to eliminate soil gas flux associated with natural soil respiration processes —Important considerations for field implementation including locations, frequency, installation procedures, and quality assurance and quality control (QA/QC) —Guidance on data evaluation and estimation of a sitewide, seasonally-weighted, annual NSZD rate
Section 4—Gradient Method	—Method description based on use of Fick's first law, including key assumptions —Guidance on installation and sampling of soil vapor monitoring points to profile concentration gradients —Procedures to estimate the D_{eff_v} and calculate O_2 influx and CO_2 efflux from soil gas concentration profiles —Discussion of the sources of data uncertainty and variability
Section 5—Passive Flux Trap Method	—Method description and use as a time-averaged CO_2 efflux measurement —Use of radiocarbon (^{14}C) to quantify the CO_2 from modern (natural soil processes) and fossil-based (petroleum NSZD) sources —Important considerations for field implementation including installation and retrieval procedures, deployment timeframe, and QA/QC samples including trip blanks and field duplicates —Explanation of lab analyses and data evaluation procedures —Discussion of the sources of data uncertainty and variability

Table 2—Document Overview and Content Reference (Continued)

Section Number and Title	Discussion Topics and Content
Section 6—Dynamic Closed Chamber (DCC) Method	—Method description and use as an instantaneous or time-averaged measurement of CO₂ efflux at individual points in time using a real-time field instrument —Important considerations for field implementation including locations, installation procedures, and QA/QC samples including field blanks and duplicates —Procedures to estimate efflux at individual locations and estimate an area-integrated site-wide NSZD rate —Discussion of the sources of data uncertainty and variability
Section 7—Emerging Methods	—Summary of methods that are nascent, but promising future advancements to NSZD monitoring technology —Description of a thermal method that estimates NSZD rates based on biogenic heat within the hydrocarbon oxidation zone —Inclusion of a monitoring program supplement for sites with CH₄ throughout the vadose zone profile, including monitoring of CH₄ efflux —Use of ¹⁴C analysis of soil vapor samples to correct for background processes using the gradient and DCC methods
Section 8—Conclusions	—Summary of guidance objectives and content —Recap of key messages with respect to design, implementation, and evaluation of NSZD —Areas of future research needs
Section 9—Bibliography	—Complete listing of published materials and citations used to develop this guidance
Appendix A—Sample Implementation Procedures	—Measuring the D_{eff_v} used for the gradient method —Installing DCC collars and passive flux trap receiver pipes —Performing CO₂ efflux measurements using a DCC Deploying and retrieving the passive flux traps —Sample field data collection forms including soil gas probe sampling log, passive flux trap field log, DCC measurement log, and soil vapor diffusion coefficient test log
Appendix B—Case Study of Three NSZD Evaluation Methods	—Case study of three NSZD estimate methods summarizing the NSZD monitoring plan, results, and data analysis —Summary of monitoring results (gas flux and NSZD rate estimates) for the gradient, passive flux trap, and DCC methods —Detailed data evaluation including anomalies, assumptions, and method comparison —Demonstration of NSZD calculations for each of the three methods

VOCs creates more CO₂ and an increase in temperature in the vadose zone. The magnitude and vertical location of the oxidation that occurs depends upon the presence of vadose zone hydrocarbon impacts, the ability for O₂ to enter the subsurface, and the lithologic profile. These byproducts are measured in various ways by the monitoring methods discussed herein and are used to estimate NSZD rates.

NOTE This is a conceptual depiction of a typical setting and thereby idealizes conditions. No indication of process magnitude is implied by font or arrow size.

Because biodegradation is ubiquitous at petroleum hydrocarbon-impacted sites, the methods described herein are applicable to a wide variety of sites. However, theory and experience dictate that there are site conditions that result in limited NSZD rates or hinder the monitoring methods and may preclude its use or require that monitoring proceed with care. Site conditions are discussed below that have been observed to have significant effects on NSZD rates or methods. Table 3 presents a listing of the site conditions, the effect on NSZD, a go or no-go general directive, and adaptations to consider prior to proceeding with a monitoring program.

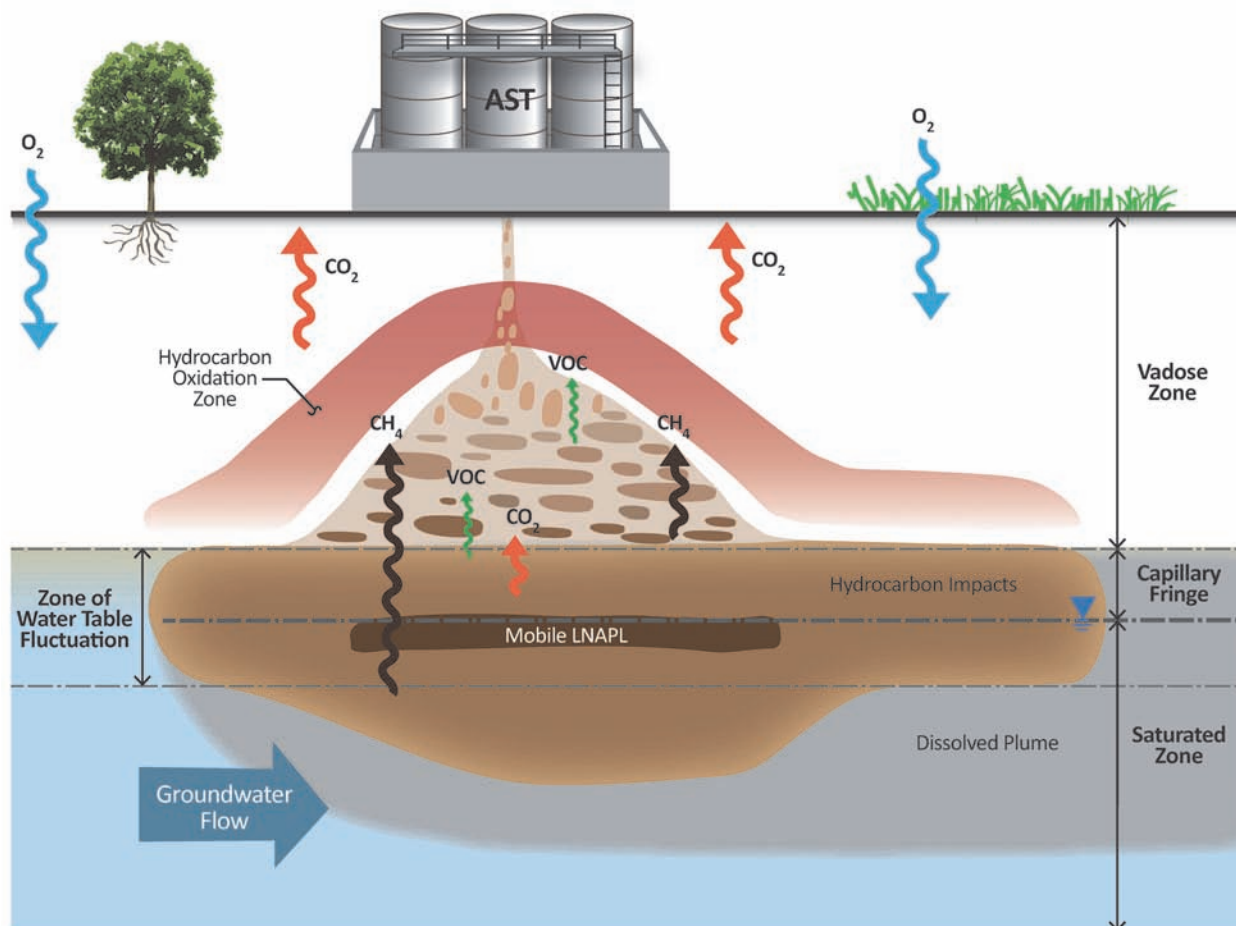


Figure 1-1
Conceptualization of Vapor Phase-Related NSZD
Processes at a Petroleum Release Site

NOTE:
This is a conceptual depiction of a typical setting and thereby idealizes conditions.
No indication of process magnitude are implied by font or arrow size.

Figure 1-1—Conceptualization of Vapor Phase-related NSZD Processes at a Petroleum Release Site

1.7.1 Site Conditions Where NSZD Monitoring is Not Recommended

Table 3 lists the few site conditions where vapor phase-related NSZD processes are limited or measurement is highly challenging using the methods described herein. These monitoring methods are not recommended at these sites. In general, it includes those sites where one or more of the key elements of NSZD depicted on Figure 1-1 (i.e. LNAPL, vadose zone, or atmospheric oxygen exchange) are not present.

1.7.2 Site Conditions Where NSZD Monitoring is Recommended with Care

Table 3 summarizes situations where vapor phase-based NSZD monitoring is applicable, but certain site conditions are of concern and implementation requires either some initial pre-screening or extra care. For example, large concentrations of CH_4 in the shallow subsurface is a good indicator that O_2 replenishment in the vadose zone is inadequate, and use of O_2 consumption or CO_2 production as a basis for estimating NSZD may be inadequate.

2 Theory of NSZD

NSZD processes occur naturally within petroleum hydrocarbon-impacted zones in the subsurface. These processes physically degrade the contaminants by mass transfer of chemical components to the aqueous and gaseous phases

Table 2-1—Summary of Site Conditions that Preclude or Affect Vapor Phase-related NSZD Monitoring

Site Condition	Effect on NSZD	Go or No-Go?	Monitoring Program Adaptation
<i>Situations Where NSZD Monitoring is Not Recommended</i>			
No identified/suspected LNAPL	Indicators of NSZD are typically only observed at sites with residual, mobile, or migrating LNAPL.	No-go	NSZD monitoring is only applicable for sites with LNAPL.
Permanently saturated and/or solid ice ground conditions	The methods discussed herein require a vadose zone with air-filled porosity for vapor transport to occur. Frozen ground may retain inter-connected air-filled pores, but solid ice will not.	No-go	The NSZD monitoring methods discussed in this guidance are applicable only for sites where vapor flux can occur.
<i>Situations Where NSZD Monitoring is Recommended with Care</i>			
Vadose zone <2 ft thick	The methods discussed herein require a minimum vadose zone thickness for vapor transport to occur and some require adequate vertical space for probe installation. Additionally, gaseous byproducts from NSZD of shallow petroleum hydrocarbon-impacted soils may not completely oxidize within the small vadose zone.	Go	Use a ground surface-based method (i.e. passive flux trap or DCC) and consider monitoring both CO ₂ and CH ₄ efflux and add stoichiometric conversions of both CO ₂ and CH ₄ to estimate the total NSZD rate (see 7.2 for details).
Large measurable concentrations of CH ₄ near ground surface (e.g. percent level as measured in a shallow probe using a landfill gas meter)	Atmospheric O ₂ exchange is insufficient to oxidize CH ₄ and convert to CO ₂ and renders the CO ₂ efflux methods of limited accuracy.	Go	Methods discussed within this guidance must be adapted to estimate NSZD rates for sites where majority of CH ₄ is not converted to CO ₂ . Consider monitoring both CO ₂ and CH ₄ efflux and add stoichiometric conversions of both CO ₂ and CH ₄ efflux to estimate the total NSZD rate (see 7.2 for details). If the CH ₄ is suspected to be an anomaly and potentially related to hydrocarbon impacts shallower than the bulk of the hydrocarbon mass (e.g. within the LNAPL smear zone), then another option is to relocate the NSZD monitoring location to assess the lateral extent of CH ₄ efflux.

Table 2-1—Summary of Site Conditions that Preclude or Affect Vapor Phase-related NSZD Monitoring

Site Condition	Effect on NSZD	Go or No-Go?	Monitoring Program Adaptation
Lack of lateral LNAPL delineation	Lack of lateral LNAPL delineation does not preclude NSZD monitoring. However, if a sitewide estimate of the NSZD rate is a data objective, then an estimate of the aerial footprint is required.	Go	Use cost-effective means to delineate the LNAPL. For example, the DCC method can be used concurrent with the CO ₂ efflux survey to delineate the lateral LNAPL extent (Sihota et al. 2016).
Intermittently flooded areas	Inundation of the ground surface and underlying vadose zone will restrict and may cut off soil gas transfer.	Go	Design the NSZD monitoring efforts to occur during dry times and consider discounting the annual estimate of NSZD if flooding is routine.
Presence of large quantities of natural organic carbon in soils such as peat and loam	Natural soil respiration may have significant effects on the soil gas profiles and gas flux. In some situations, organic matter may even create CH ₄ , in addition to consuming O ₂ and creating CO ₂ .	Go	If organic rich zones are discontinuous over the LNAPL footprint, then avoid NSZD monitoring in zones containing it. Otherwise, utilize advanced background correction methods such as ¹⁴ C.
Ground cover such as asphalt, concrete, compacted soil, or geotextiles	These types of ground cover restrict O ₂ exchange with the subsurface and, if significant enough, will limit CH ₄ oxidation. Additionally, they limit applicability of ground surface-based methods such as the passive flux trap and DCC. Penetration will create a chimney effect that will disturb natural soil gas patterns and result in high-biased efflux results.	Go	Verify the soil gas concentration profile to demonstrate that ample O ₂ is penetrating the subsurface through diffusion gradients. If elevated CH ₄ is present in shallow soils above the hydrocarbon impacts, then include CH ₄ flux monitoring and add stoichiometric conversions of both CO ₂ and CH ₄ flux to estimate the total NSZD rate (see 7.2).
Active ongoing remediation using soil vapor extraction (SVE)	SVE significantly alters the soil gas transport regime through advection resulting in a net inflow of gases at the ground surface. This, in turn, disturbs the soil gas profiles above the petroleum hydrocarbon-impacted soils and invalidates assumptions with the all NSZD monitoring methods.	Go	Shut down the SVE system for a period of time necessary to allow re-equilibration of soil gas concentration profiles. After a series of routine field measurements verifies stability, then the NSZD monitoring can begin. Note that the duration for re-equilibration can vary greatly, from days to months.
Regionally elevated CH ₄ and/or CO ₂ flux from deep geologic fossil-based sources	"Background" sources of CH ₄ and/or CO ₂ flux can also include deep petroleum or natural gas reservoirs underlying the LNAPL source zone of concern. Modified correction is needed to exclude these other, non NSZD-related sources.	Go	Prescreen the background fossil-based gas flux outside the LNAPL footprint. Consider performing ¹⁴ C analysis in background areas to quantify the fossil-based fraction of CO ₂ derived from underlying petroleum reservoirs and using it as a basis for correction.
Large depth to LNAPL (e.g. >100 ft below ground surface [bgs])	Soil vapor mixing in the large vadose zone above the hydrocarbon impacted soil may obscure/dilute the ground surface efflux of CO ₂ and cause inaccuracies in these methods.	Go	Use non-ground surface-based NSZD monitoring methods such as the gradient method or other emerging methods such as thermal monitoring (see 7.1).
Cold climate (i.e. ambient temperatures sustained below freezing for long durations)	Cold/frozen subsurface conditions may stall biodegradation, limit vapor transport, and reduce NSZD rates at sites with shallow LNAPL impacts (Sihota et al. 2016).	Go	Monitor seasonal changes to determine the effect of sub-freezing ambient temperatures on subgrade NSZD rates.

Table 2-1—Summary of Site Conditions that Preclude or Affect Vapor Phase-related NSZD Monitoring

Site Condition	Effect on NSZD	Go or No-Go?	Monitoring Program Adaptation
Saturated silt/clay geology overlying petroleum hydrocarbon-impacted soils	Low-permeability, saturated soils may restrict soil gas movement. Note that this is a similar effect as imposed by ground cover such as asphalt or compacted soil.	Go	Verify the soil gas concentration profile to demonstrate that ample O ₂ is penetrating the subsurface through diffusion gradients. If elevated CH ₄ is present in shallow soils above the hydrocarbon impacts, then include CH ₄ flux monitoring and add stoichiometric conversions of both CO ₂ and CH ₄ flux to estimate the total NSZD rate (see 7.2).
Natural CO ₂ generation from calcareous sands or dissolution of carbonate rock	CO ₂ flux from “background” sources can also include soil/ rock with carbonates. Modified correction is needed to exclude these other, non-soil respiration-related, sources of CO ₂ .	Go	Characterize the background CO ₂ flux using isotopic methods such as ¹⁴ C, which will exclude CO ₂ from carbonate-containing geologic materials

where they are biologically broken down. This section describes the various aqueous- and vapor phase-related processes associated with NSZD and introduces the methods that can be used to quantitatively measure NSZD.

2.1 Attenuation Processes

After a release into the environment, petroleum hydrocarbon constituents in LNAPL undergo various degradation reactions. These reactions include: sorption onto subsurface solids, dissolution into groundwater followed by biodegradation in the saturated zone, and volatilization and biodegradation in the vadose zone (Kostecki and Calabrese 1989; NRC 1993; NRC 2000; Johnson et al. 2006).

Within the LNAPL-impacted soil in the saturated zone, biodegradation occurs via methanogenesis and leads to vertical soil gas transport (Weidemeier et al. 1999), resulting in generation and subsequent transport of CH₄ and CO₂ to the vadose zone. Within the overlying hydrocarbon-impacted vadose zone, where conditions remain anaerobic, these processes continue. In the overlying oxic vadose zone, the LNAPL, CH₄, and sorbed and volatile hydrocarbons are aerobically biodegraded reducing or removing O₂ and VOCs from the soil gas, adding CO₂, and releasing heat to the soil.

2.1.1 NSZD Processes in the Saturated Zone

Following Molins et al. (2010), the saturated zone is considered to include the petroleum hydrocarbon-impacted region surrounding the water table including the capillary fringe. It typically contains LNAPL and sorbed phase hydrocarbons and is characterized by high water- and low vapor-phase saturations. The interface of the saturated zone, especially the top portion of it containing LNAPL, is often dynamic due to fluctuations in the water table elevation. If LNAPL is present at high enough saturations, an LNAPL smear zone can be created by the water table fluctuation. The degree of saturation of the smear zone is variable depending upon the elevation of the underlying water table.

The key NSZD processes occurring in the saturated zone include the following:

- dissolution of soluble LNAPL and sorbed-phase constituents;
- biodegradation of solubilized hydrocarbons via aerobic respiration, nitrate reduction, iron reduction, manganese reduction, and sulfate reduction;
- production of dissolved biodegradation byproducts including CO₂, Fe²⁺, Mn²⁺, CO₂ and CH₄;

- biodegradation of solubilized hydrocarbons via methanogenesis;
- production of dissolved and gaseous byproducts including CH_4 and CO_2 .

Figure 2-1 shows the key source zone dissolution and biodegradation mass depletion processes in the saturated and overlying capillary fringe zones.

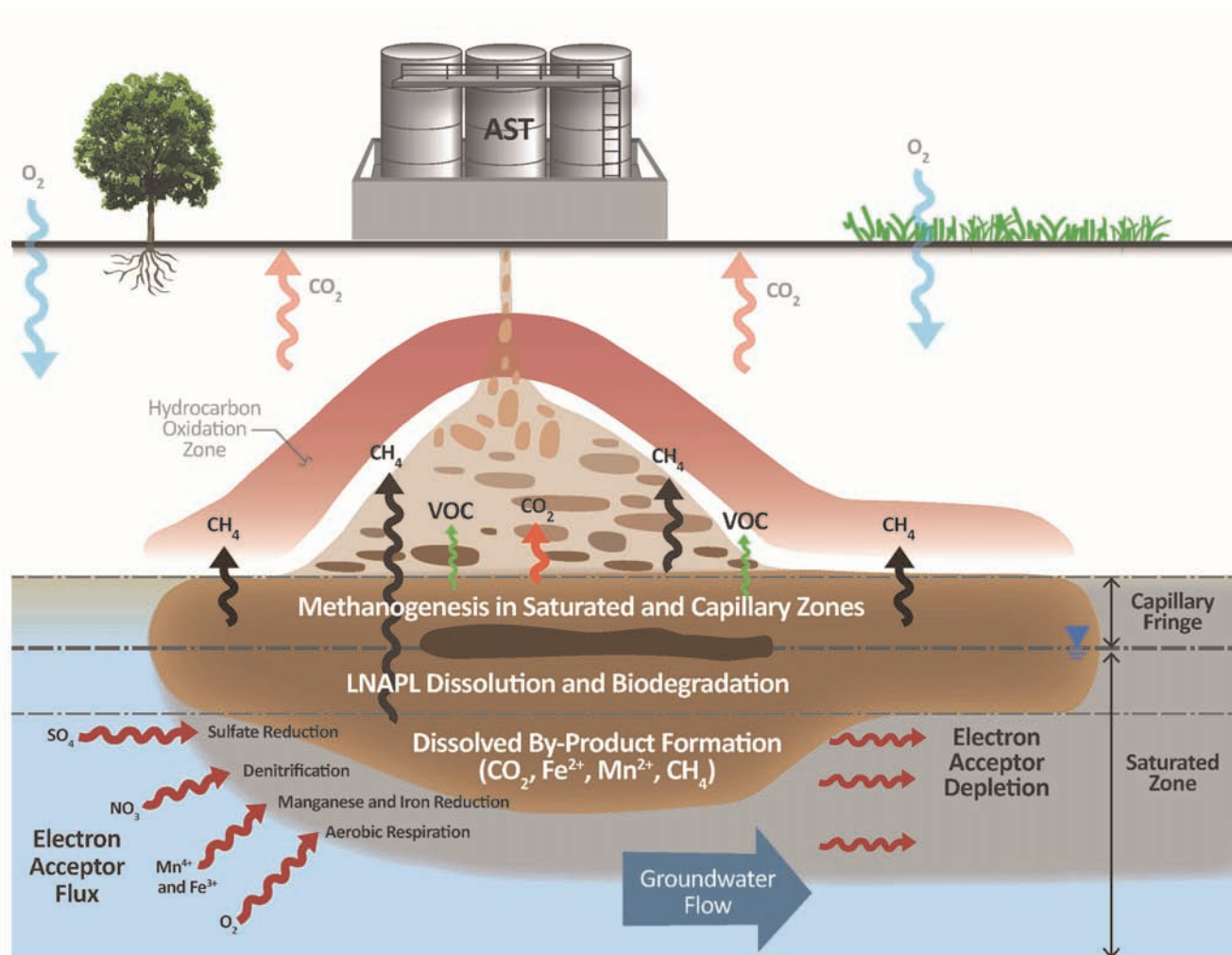


Figure 2-1—Conceptualization of Saturated Zone NSZD Processes

NOTE Process arrows unrelated to the saturated zone are intentionally screened back.

Following Raoult's law, submerged petroleum hydrocarbon source zones dissolve into groundwater based on the mole fraction and pure chemical solubility of the individual components (Banerjee 1984). Via dissolution of the LNAPL, mass is lost as dissolved components biodegrade or exit the source zone with groundwater flow (Kostecki and Calabrese 1989). Upon partitioning into the aqueous phase, the chemical components become available for biodegradation. Microbial biodegradation of dissolved petroleum hydrocarbon plumes in groundwater is well documented (NRC 1993). It can occur through various terminal electron accepting reactions. Decreases in dissolved O_2 , nitrate (NO_3^-), and sulfate (SO_4^{2-}) as well as increases in dissolved iron (Fe^{2+}), manganese (Mn^{2+}), CO_2 , and CH_4 in groundwater downgradient of the source zone provide evidence of saturated zone biodegradation (NRC 2000). Naturally occurring groundwater geochemistry often controls the electron acceptor supply and the dominant terminal electron acceptor processes. The microbes preferentially use O_2 as an electron acceptor. As O_2 is

depleted, the other electron acceptors are used and, when they are consumed, the saturated zone generally proceeds to a methanogenic state. In other situations, the availability of electron acceptors may not be limiting. The dissolved phase-related NSZD processes are discussed further in ITRC (2009a).

At many petroleum release sites, the biodegradation processes in the saturated zone produce an excess of gaseous byproducts and both CO₂ and CH₄ gas will be observed in the overlying vadose zone. At sites where methanogenesis dominates, a relatively larger accumulation of CH₄ may be observed. On the contrary, where the system is not electron acceptor limited, methanogenesis may not dominate and a relatively larger accumulation of CO₂ may be observed. The soluble portion of the biodegradation byproducts (including CO₂ and CH₄) dissolve and migrate away from the source zone via groundwater advection. The remainder of the produced CH₄ and CO₂ partitions into the vapor phase and migrates into the vadose zone by volatilization, off-gassing, and/or ebullition.

Under anaerobic conditions and facilitated by methanogenic microorganisms, petroleum hydrocarbons (e.g. octane C₈H₁₈) react with water (H₂O) to create CO₂ and CH₄ gases via Equation 2.1 (adapted from US EPA 1998):



Methanogenesis

At the U.S. Geological Survey Bemidji Crude-Oil Research Project Site near Bemidji, Minnesota (Bemidji site, <http://mn.water.usgs.gov/projects/bemidji/index.html>), a mass balance modeling simulation estimated that approximately 98 % of the carbon generated from petroleum hydrocarbon biodegradation reactions is released as gas (i.e. CO₂) across the ground surface while the remaining carbon enters the saturated zone via groundwater dissolution (Molins et al. 2010).

An NSZD study at the former Guadalupe oil field in California (Lundegard and Johnson 2006), for example, showed that source zone mass losses associated with dissolution/biodegradation in the saturated zone as manifested by changes in dissolved byproducts were approximately two orders of magnitude lower than losses associated with vapor phase-related byproducts of source zone biodegradation. The vapor phase-related NSZD processes were predominantly quantified by the transport of CH₄ to the vadose zone from biodegradation of petroleum-impacted soil occurring in both the saturated and vadose zones.

Saturated zone offgassing and ebullition occur because CH₄ has a high Henry's law constant (0.66 atm m³/mol at 25 °C), is relatively insoluble (22 mg/L at 25 °C), and CH₄ production is significant and comparable to an anaerobic sludge digester at a wastewater treatment plant (Molins et al. 2010; Amos et al. 2005). When CH₄ accumulates in groundwater, gas bubbles form, CH₄ and CO₂ partition into the gas bubbles, are buoyantly transported through the saturated zone, and in turn this leads to ebullition of CH₄ and CO₂ into the vadose zone (Amos and Mayer 2006). In this way, the gases produced from biodegradation of the LNAPL are transferred to the vadose zone. The CH₄ and CO₂ observed in the vadose zone can have origins from methanogenesis in the saturated, capillary, and vadose zones where anaerobic biodegradation of petroleum hydrocarbons is occurring.

2.1.2 Vapor Phase-related NSZD Processes

Figure 2-2 depicts the basic components of NSZD mass loss processes as manifested by changes in the vapor phase in the vadose zone. For the reasons discussed above, the focal interest to this guidance are the vapor phase-related NSZD processes. The key vapor phase-related petroleum hydrocarbon source zone NSZD processes include the following:

- volatilization of LNAPL and sorbed hydrocarbon constituents;
- shallow aerobic biodegradation of volatilized hydrocarbons partitioned into soil moisture,
- production of gaseous CO₂ from hydrocarbon oxidation;

- aerobic oxidation of CH_4 derived from saturated zone processes,
 - production of gaseous CO_2 from CH_4 oxidation;
- other non-NSZD sources of CO_2 production and O_2 consumption that need to be accounted;
 - production of CO_2 from respiration of natural organic matter, such as peat and humic matter,
 - production of CO_2 from root zone respiration in shallow soil.

Similar processes as those described above for the saturated zone occur in the anaerobic hydrocarbon-impacted soil in the vadose zone including the production of CH_4 and CO_2 gases. Additionally, where the vadose zone contains O_2 , aerobic biodegradation and hydrocarbon oxidation occur. Volatilization also occurs following the four-phase partitioning theory (soil, LNAPL, water, air); the various hydrocarbons in the vadose zone will volatilize into the soil vapor based on its mole fraction and pure chemical vapor pressure of the individual components. As discussed in Chaplin et al. (2002), volatilization of hydrocarbons from LNAPL is most important in the early stages of attenuation immediately after a release into the environment and becomes a less significant process as the LNAPL ages.

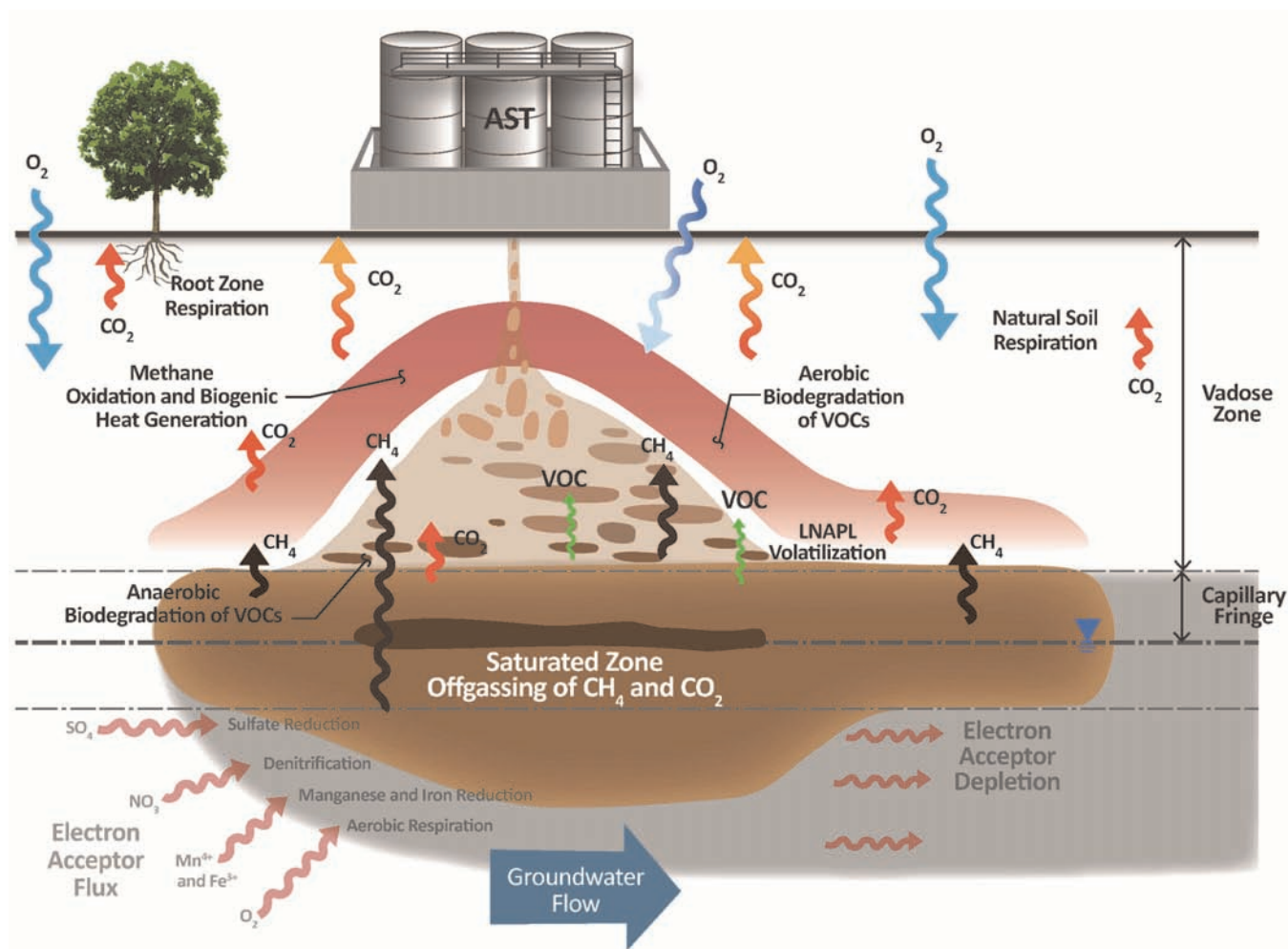


Figure 2-2—Conceptualization of Vapor Phase-related NSZD Processes

2.1.2.1 Vapor Transport Processes in the Vadose Zone

The gases generated by NSZD (of most interest in this document are CH₄, CO₂, and VOCs) will be transported outward by diffusion, ebullition, and advection. Diffusion affects the distribution of soil vapors when there are spatial differences in chemical concentrations in the soil gas. The net direction of diffusive transport is toward the direction of lower concentrations, typically toward the ground surface. The rate of diffusion depends on the individual petroleum hydrocarbon constituents' effective soil vapor diffusion coefficient ($D_{eff,v}$) and the air-filled porosity of the soil. Diffusive processes are typically faster in sandy soil types with lower moisture content, as these soils have greater air-filled effective porosity values (ITRC 2009a).

Soil gas movement in the vadose zone near LNAPL source zones is also driven by ebullition (buoyant gas bubbles) and advective forces (the movement of soil gas from areas of high pressure to areas of lower pressure). Although in unimpacted areas the dominant process for vapor transport is typically diffusion (US EPA 2012), many different site conditions can affect advective movement of soil gas in the vadose zone. Water table fluctuations, land surface-based topography and wind, the presence of more permeable subsurface pathways, either natural or artificial, and the gaseous biodegradation reaction byproducts themselves can cause pressure gradients and drive soil vapor advection (Wealthall et al. 2010). Additionally, even thin lower permeability heterogeneous soil layers can affect the transport of soil gas through the vadose zone significantly (DeVaul et al. 2002). Advection is generally limited to areas with spatial differences in soil gas pressure in or near the ground surface, immediate vicinity of buildings, utility corridors, and wherever CH₄ generation from anaerobic degradation is sufficiently high (e.g. near some landfills, some locations with degrading fuels) (US EPA 2015). This latter condition was assessed at the Bemidji crude oil release site and results indicated that diffusion remained the dominant transport mechanism (Molins et al. 2010; Sihota and Mayer 2012; Sihota et al. 2013). Advection contributed up to 15 % of the net CH₄ fluxes.

2.1.2.2 Biodegradation Processes

During transport, vapor phase hydrocarbons can partition into the aqueous phase pore water, where they are susceptible to biodegradation (Ostendorf and Kampbell 1991). The rate of biodegradation in situ will be chemical-specific (i.e. chemicals have different degradation rates even within a similar microbial environment), will be site-specific (i.e. the microbial environment will depend upon soil moisture, nutrient and O₂ levels, and the chemical mixture, among other factors [Holden and Fierer 2005]), and may be location-specific (i.e. the microbial environment can change over time and space due to variations in soil moisture, nutrient, and O₂ levels). In some cases, subsurface oxygenation and aerobic biodegradation in the vadose zone can impede vapor migration significantly (US EPA 2015). Where aerobic degradation of hydrocarbons occurs, gaseous CO₂ will be produced. Where anaerobic biodegradation occurs, both CH₄ and CO₂ will be produced.

As discussed above, CH₄ derived from saturated zone volatilization, offgassing, and ebullition and anaerobic biodegradation of petroleum hydrocarbon constituents in the vadose zone will be transported vertically upwards through the vadose zone via diffusion, and to a lesser extent via advection. Countercurrent to the upward CH₄ transport is the downward transport of O₂ from the atmosphere. Where the CH₄ and O₂ meet, it creates a relatively thin hydrocarbon oxidation zone where CH₄ and petroleum hydrocarbon VOCs (if present) are converted to CO₂ according to Equation 2.2 (Davis et al. 2009; Revesz et al. 1995):



Methane Oxidation

The location of the hydrocarbon oxidation zone is controlled by the limitations of O₂ ingress through the ground surface and soil and the top elevation of the underlying hydrocarbon-impacted soil. For example, at the Bemidji site, the oxidation zone was approximately 1 ft thick and was identified approximately 8 ft bgs within the upper portion of a low permeability layer via significant increases in CO₂ and decreases in CH₄ concentrations, 12C enriched isotopes, and a sharp transition between high and low partial pressures of CH₄ (Sihota and Mayer 2012). Work at a former refinery in Wyoming showed that the top of the oxidation zone fluctuates seasonally due to variations in the inward

fluxes of O_2 and outward fluxes of CH_4 (Irianni-Renno 2013). Regardless of the depth and thickness of the oxidation zone, the reaction in Equation 2.2 necessitates that the stoichiometric ratio of the O_2 and CH_4 fluxes remain constant.

Of the biogenic gases that are produced by the NSZD processes in the vadose zone (CO_2 and CH_4), efflux across the ground surface is dominated by CO_2 , with CH_4 emissions generally being insignificant (Sihota and Mayer 2016). At the Bemidji site, modeling-based estimates suggest that greater than 98 % of the carbon produced by biodegradation reactions was released across the ground surface as CO_2 efflux while the remaining carbon entered the saturated zone via groundwater dissolution (Molins et al. 2010).

2.1.2.3 Methanogenesis

Unlike other anaerobic biodegradation reactions, methanogenesis isn't limited by the need of external electron acceptors. Methanogenesis has been shown to occur by CO_2 reduction in the soil moisture within the vadose zone and acetate fermentation (Revesz et al. 1995). Thermodynamically, the reaction is limited by the hydrogen (H_2) concentration in groundwater (Dolfing et al. 2008). Methanogenesis via the acetate-fermentation reaction can be limited by acetate buildup (Wilson et al. 2016a). The reaction can also be limited by the availability of nutrients (Bekins et al. 2005) and the reaction rate limited by the temperature of groundwater (Zeman et al. 2014).

At the Guadalupe oil field, agreement between the hydrocarbon-equivalent degradation rates calculated from the downward diffusing O_2 and the upward diffusing CH_4 at the top of the hydrocarbon-impacted soil provided a clear indication that methanogenesis is an important process in the vapor phase-related source zone NSZD processes (Lundegard and Johnson 2006). Following this finding and assuming a mature LNAPL source zone, then if the rate of the methanogenesis is sufficient to completely deplete O_2 above the petroleum hydrocarbon impacted soils, then CH_4 flux could be used to closely approximate the rate of NSZD at the site.

At the Bemidji, Minnesota crude oil spill site, a mass balance modeling simulation estimated that approximately 85 % of the oil degradation occurring in the vadose and saturated zones takes place by methanogenesis (Molins et al. 2010).

Based on studies at the Guadalupe and Bemidji sites, methanogenesis has been demonstrated to be an important process responsible for determining the rate of NSZD at a site. However, the magnitude of methanogenesis is variable and should be assessed on a site-specific basis. At the Bemidji site, for example, CH_4 only gradually appeared in the vadose zone after the crude oil release. It took between 10 and 16 years for methanogenesis to become the dominant hydrocarbon degradation process (Molins et al. 2010).

2.1.3 Composite Conceptualization of NSZD

A composite summary of the physical, chemical, and biological NSZD processes in the saturated and vadose zones is shown in Figure 2-3. This is a conceptual depiction of a typical NSZD setting and thereby idealizes conditions. No indication of process magnitude is implied by font or arrow size. The conceptualization is most relevant to a middle- to late-stage LNAPL source zone (Tracy 2015). That is, when microbiological processes achieve a pseudo-steady state after methanogenesis is well-established. A middle-stage condition occurs when LNAPL migration and expansion ceases and is offset by natural losses. A late-stage condition occurs when NSZD has removed the bulk of LNAPL and the remaining hydrocarbon exists as sparse residual LNAPL.

For the purposes of this document, two typical scenarios are described. Scenario A contains hydrocarbon-impacted soils above the saturated zone and no near-surface vegetation. Scenario B essentially has a "clean" vadose zone above the LNAPL smear zone and contains near-surface vegetation along with a root zone. The presence/absence of vadose zone impacts has an important effect on the distribution of vapors. As shown on Figures 2-3A and 2-3B, the effect is the addition of an anaerobic vadose zone (Zone 3), which results in an upward shift in the location of the hydrocarbon oxidation zone (Zone 2).

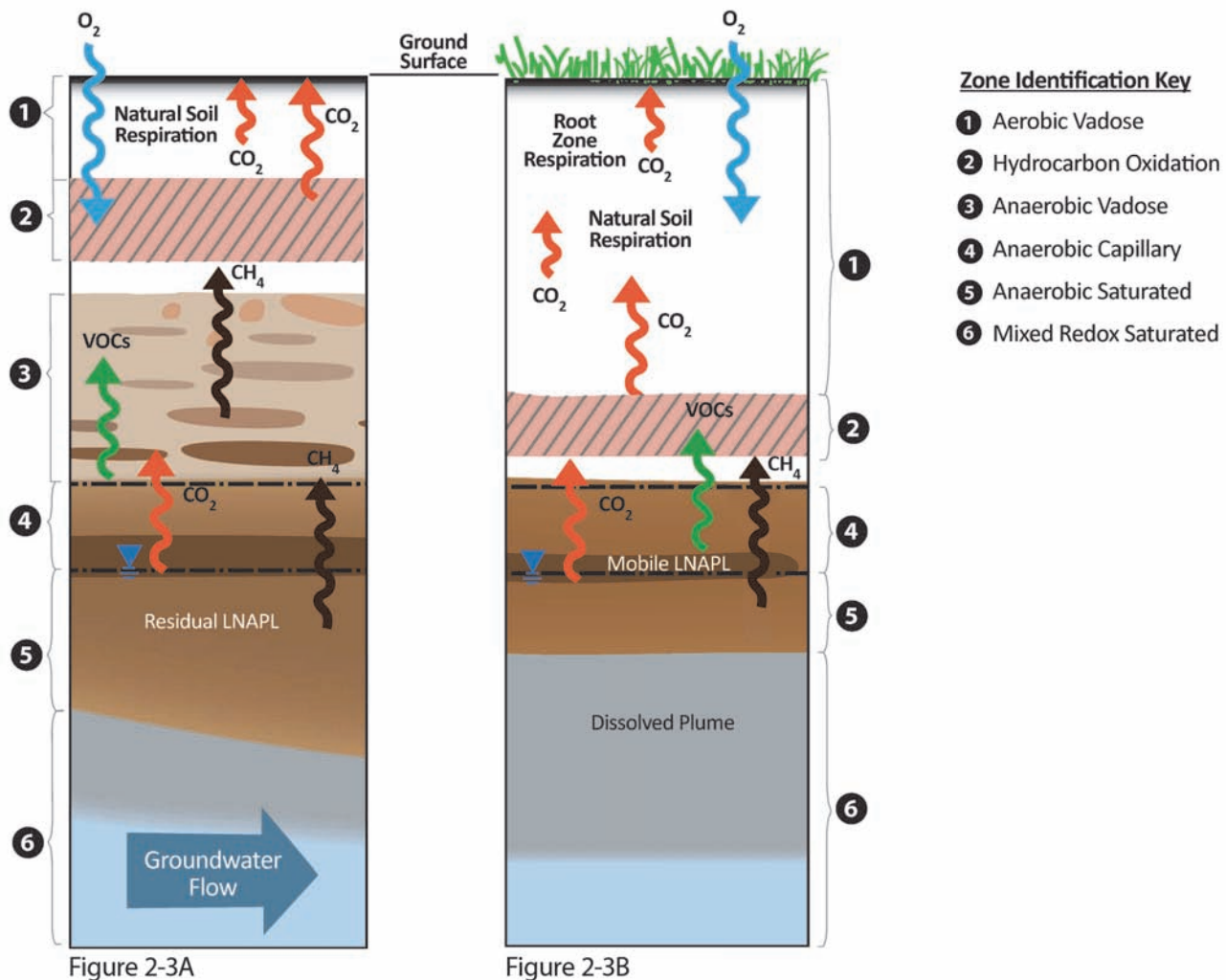


Figure 2-3—Conceptualization of Vapor Phase-related NSZD Processes (a) with and (b) without Hydrocarbon Impacts in the Vadose Zone

For the purposes of illustration, the subsurface can be divided into six zones corresponding to different conditions of water saturation, hydrocarbon source mass, redox state, and biodegradation reactions.

- **Zone 1.** Unimpacted, aerobic, vadose zone where O_2 is transported downward and the efflux of CO_2 from subsurface NSZD processes is mixed with CO_2 that is created by decomposition of natural organic matter in the soil and root zone respiration. The amount of CO_2 generated in this region varies significantly depending on the fraction organic carbon in the soil (DeVaul 2007) and type of ground surface cover (e.g. vegetated, woodland, gravel). The amount of CO_2 created in Zone 1 of Scenario B is expected to be larger due to the presence of surface vegetation and a root zone.
- **Zone 2.** Hydrocarbon oxidation zone where downward transported O_2 meets upward migrating CH_4 and VOCs and creates an oxidation reaction where the hydrocarbons are converted to CO_2 and heat. This zone may contain hydrocarbon-impacted soils; if it does, then a zone of aerobic petroleum biodegradation is present which creates more CO_2 . The rate of CH_4 oxidation is limited by the rate of O_2 diffusion from atmosphere, which is a function of soil permeability, air-filled porosity, and moisture content.

- **Zone 3.** Hydrocarbon-impacted, anaerobic, vadose zone where a residual mass of LNAPL and sorbed hydrocarbons in soil forms a distinct unsaturated zone absent of O_2 above the capillary fringe. Methanogenesis dominates the mass loss processes in this region and it creates a measurable amount of CH_4 that exits via ebullition (nearest capillary fringe) and volatilization. Volatile petroleum hydrocarbons will also be emitted from this zone.
- **Zone 4.** Hydrocarbon-impacted, anaerobic, partially saturated, capillary fringe zone where, in conjunction with the underlying Zone 5, the bulk of the LNAPL mass resides. Its vertical location is subject to water table fluctuations. Methanogenesis dominates the mass loss processes in this region and it creates a measurable amount of CH_4 and CO_2 that exit the region via volatilization, offgassing, and ebullition. The methanogenic reaction is limited by CO_2 electron acceptor, H_2 in groundwater, nutrients, and/or temperature.
- **Zone 5.** Hydrocarbon-impacted, anaerobic, saturated zone where, in conjunction with the overlying Zone 4, the bulk of the LNAPL mass resides. Various processes are occurring in this zone that create dissolved and vapor phase biodegradation byproducts. In particular, methanogenesis dominates the mass loss processes in this region and it typically creates an excess amount of CH_4 and CO_2 that exits the region via offgassing. The methanogenic reaction is limited by CO_2 electron acceptor, H_2 in groundwater, nutrients, and/or temperature.
- **Zone 6.** Dissolved hydrocarbon-impacted, mixed redox state, saturated zone where a relatively small hydrocarbon mass is submerged below the water table and degradation is driven by the availability of electronic acceptors (e.g. NO_3 for nitrate reduction, SO_4 for sulfate reduction). In general, only soluble amounts of CH_4 and CO_2 are produced along with small amounts of dissolved biodegradation byproducts.

2.2 Thermal Signatures of Biodegradation

Hydrocarbon biodegradation reactions are exothermic—they produce energy. Most of this energy is used by microbes to grow and to fuel their metabolism, but some is given off as heat. The microbial communities present in soil and groundwater at LNAPL release sites adapt and acclimate as the LNAPL degrades over time. For example, as the more volatile hydrocarbon constituents leave the LNAPL during the early-stages of a release, volatilization rates decrease and the most significant mass loss mechanisms transition to biodegradation (Chaplin et al. 2002). As the subsurface makes this transition, the bioactivity in the source zone changes to acclimate to sequentially less thermodynamically favorable conditions as electron acceptors are depleted, ultimately resulting in methanogenic conditions. In a strict sense, the dynamic microbiological condition will likely continue until middle- to late-stage LNAPL source zone conditions are achieved (see 2.1.3). For the purposes of conceptualization, it is assumed that a microbial population undergoing middle- to late-stage NSZD stabilizes and achieves a pseudo-steady state. Under such a pseudo-steady state, microbial growth rates are relatively small, and most of the energy produced is given off as heat to the surrounding soil. The resulting thermal flux is proportional to the NSZD rate, as the heat of these reactions is stoichiometrically related to the extent of reactions by thermodynamic relationships. Previous laboratory research using calorimeters has confirmed that microcosm studies undergoing degradation reactions generate a stoichiometric amount of heat (for example, Braissant et al. 2010).

The biodegradation of petroleum in soils is analogous to a compost pile, as it is a process in which microorganisms generate heat, and this heat is simultaneously transferred to the surroundings. The interaction of surrounding ambient temperatures, heat released from biodegradation, and the heat transfer processes determine local soil temperatures. The maximum amount of heat generated from biodegradation will occur where O_2 is being depleted from the soil gas (i.e. where aerobic reactions are occurring and depleting O_2). This occurs within the hydrocarbon oxidation zone, Zone 2 as shown in Figures 2-3A and 2-3B, and results from the reaction shown on Equation 2.2. Less heat will be released if the rate of microbial biodegradation is low (i.e. limited by temperature, nutrients, or other environmental factors). Sensitivity of microbes to local temperatures ultimately determines the overall rate of hydrocarbon biodegradation in soils with larger NSZD rates generally occurring at higher temperatures. Empirical site data identified that measured petroleum NSZD rates at a field site correlated with groundwater temperatures (for example, McCoy et al. 2014).

Warren and Bekins (2015) investigated biogenic heat released from NSZD at the Bemidji site and found temperatures above the crude oil body in the unsaturated zone were up to 2.7 °C higher than temperatures outside of the LNAPL footprint. Enthalpy calculations and observations demonstrated that the temperature increases primarily resulted from aerobic CH₄ oxidation in the unsaturated zone above the oil. CH₄ oxidation rates at the site independently estimated from ground surface CO₂ efflux data were comparable to rates estimated from the observed temperature increases.

The thermal signature of NSZD is an area of active research and is further described in 7.1.

2.3 Estimation of Natural Source Zone Depletion

A vertical zonation of NSZD biodegradation processes and the associated geochemical gradients have been summarized. CH₄ is generated in the saturated zone and transported to the vadose zone. Within the vadose zone there is potential for additional methanogenesis to occur if hydrocarbon-impacted soil is present. The most important processes are aerobic oxidation of CH₄, volatile hydrocarbons, and hydrocarbon-impacted soil. NSZD rates are reflected in the development of O₂ and CO₂ concentration gradients. With soil being an open system, the production of reaction byproducts (CO₂) and intermediates (CH₄) and the consumption of reactants (O₂) results in transport of these constituents. The transport results in measurable soil gas flux that can be used to stoichiometrically estimate the NSZD rate. The method to calculate the NSZD rate based on the measured gas flux is discussed in detail in Section 3.

3 General NSZD Evaluation Considerations

This section contains detailed information for those at the inception of planning an NSZD monitoring program. It includes discussion of general topics that apply to all monitoring methods including important program design elements, field implementation procedures, and data evaluation notes. Additional method-specific considerations and procedures follow in Sections 4 through 6.

3.1 Program Design Considerations

Regardless of the methods used, an NSZD monitoring program contains various design elements important for success. They are described in detail in this section.

3.1.1 NSZD-related LNAPL Conceptual Site Model Development

An LCSM forms the starting place for design of an NSZD monitoring program. LCSM development is described in detail elsewhere (ASTM 2006). Table 3-1 presents a summary of the key elements of an LCSM as they relate to NSZD monitoring. The below minimum information should be collected prior to design of an NSZD monitoring program.

As Table 3-1 shows, implementation of an NSZD monitoring program does not require information beyond what is normally collected as part of petroleum hydrocarbon site characterization and remediation. At most sites, existing information can be reviewed and compiled into a format that is useful for NSZD monitoring design.

3.1.2 Data Use Objectives and Scope of Monitoring

Like any environmental monitoring program, it is important to establish data use objectives prior to implementation of an NSZD monitoring program. The scope and duration of the field effort will vary depending on the ultimate data use. Table 3-2 presents the spectrum of data use objectives from simple desktop assessment to a more complex long-term evaluation. It is intended to highlight the basic monitoring program parameters and how each data use objective can impact the scope and duration of the effort.

Data quality must also be considered on a site-specific basis. Data quality should increase as the data use becomes more critical to remedial decision making. For example, multiple NSZD monitoring methods or multiple monitoring events may be considered to assess variability and seasonality of NSZD rates on sites where the data will be used for

Table 3-1—Summary of Key LCSM Elements and Their Relations to NSZD

Element of LCSM	Relation to NSZD Monitoring Design
Lateral extent of LNAPL	Forms the area of the NSZD survey-monitoring outside the LNAPL footprint can generally be considered background if there are data to document no hydrocarbon impacts at depth. Multiple releases/separate LNAPL bodies on the same facility or deep LNAPL occurrence with tortuous soil gas transport pathways, for example, require adaptation of the NSZD monitoring program.
Vertical extent of LNAPL	NSZD occurs only in petroleum hydrocarbon-impacted areas. The rate may vary based on the amount of LNAPL present and where it occurs in the subsurface, although these effects remain a subject of study (see 8.2).
Type of LNAPL and fluid density	Conversion of biodegradation byproduct vapor flux to an NSZD rate requires a stoichiometric conversion using a hydrocarbon representative of the LNAPL mixture. Conversion to a volumetric-based NSZD rate requires the LNAPL density.
Depth to groundwater and water table fluctuation	NSZD monitoring using these vapor phase-related methods can only be performed in the unsaturated zone above the hydrocarbon impacted soil. The effects of LNAPL submergence on NSZD rates is uncertain. Consider timing NSZD measurements at extremes of seasonal high and low water table for site-specific assessment of this potential effect.
Ambient temperature/climate	At sites with shallow petroleum hydrocarbon source zones (e.g. <20 ft [Sweeney and Ririe 2014]) or significant changes in groundwater temperatures, NSZD rates may vary with seasonal change in soil temperatures. At these types of sites, ambient temperature changes affect soil temperature. Effects of root zone activity on shallow soil gas profiles and flux is highest during the warmer, vegetation growing season. Competent ground ice may limit shallow soil vapor flux. Ground frost is often permeable and does not necessarily restrict soil gas exchange with the atmosphere. Consider the temperature and water table elevation effects in parallel as there can often be optimum times to measure when water tables are lowest and soil temperatures highest.
Depth to top of hydrocarbon impacts in soil	The top of the hydrocarbon impacts will drive soil gas concentration profiles and determine where gradient method monitoring should be located. Layers of shallow zones of petroleum in soil, separated by “clean” soil, above the bulk of the hydrocarbon mass in the LNAPL smear zone, for example, may confound data interpretation from the gradient method.
Soil type and moisture content	Movement of gases (i.e. VOCs, O ₂ , CO ₂ , and CH ₄) is more limited in finer-grained formations and soils with a higher moisture content. Limitation of O ₂ influx will limit NSZD rates. Bedrock presence does not preclude NSZD monitoring, but affects method selection.
CH ₄ concentration in shallow soil gas	Presence of elevated CH ₄ at or near ground surface indicates soil gas exchange is limited, CH ₄ oxidation is incomplete. CH ₄ will drive method selection to potentially include measurement of CH ₄ flux.
LNAPL distribution and hydrostratigraphy	LNAPL can occur in the subsurface under unconfined, confined, or perched conditions. Each of these conditions could affect the NSZD rates.

remedial technology selection and/or decision document purposes. On the contrary, a single event using few monitoring locations may be appropriate for a project team looking only to ascertain the relative effectiveness of NSZD with respect to other remedial options.

To keep data quality in perspective, however, as discussed further throughout this document, NSZD rates vary geospatially and temporally. In addition, each monitoring method has its own inherent assumptions and data

Table 3-2—Spectrum of Data Use Objectives and the Associated Scope of NSZD Monitoring

Data Use Objective	Scope	Onsite Monitoring Duration
Screening-level (qualitative) assessment of NSZD	Desktop, theoretical analysis using pre-existing data as described in 3.1.4.1	No onsite monitoring
NSZD spot check or affirmation of occurrence	One event, single hydrocarbon-impacted location, during warmer time of year	~1 week
NSZD snap shot in time	One event, multiple locations, during time of year with mean ambient temperature (e.g. late fall or early winter for a temperate climate [Sihota et al. 2016])	~1 month
Assessment of range in NSZD rates	Two events, multiple locations, to coincide with extremes in seasonal changes in temperature and/or water table elevation (Sihota et al. 2016)	~6-8 months
Annual NSZD estimate	Two or more events, multiple locations, to monitor seasonal high and low and intermediate times with conditions closer to annual mean value temperature and water table elevation. Fewer events needed for monotonic climates than for temperate climates.	~1 year
Long-term NSZD monitoring	Variable scope options dependent on pre-existing understanding of NSZD rates and actual rate of NSZD, ranges from annual monitoring to 5-10 year intervals. For example, if the initial evaluation adequately characterized the sitewide NSZD rate, then long-term monitoring may only be needed at one or two key locations.	Long-term for the duration of an NSZD remedy

interpretation challenges. These are noted in the data evaluation subsections of each method description of this document (see Sections 4 through 6). The end result of this compounded variability is a value for NSZD that could be considered an order-of-magnitude estimate. The practitioner is advised to carefully consider the sources of variability and tailor their NSZD monitoring program objectives and procedures accordingly.

3.1.3 Optional Pre-design Characterization

In addition to the LCSM elements described above, some project teams may find a pre-design soil gas survey informative to help improve understanding of site conditions and refine design of the NSZD monitoring program.

One option includes collection of soil gas samples from the subsurface above the water table. This can be performed using existing monitoring wells with screens that are partially open to the vadose zone. The methods to perform this sampling are described in ITRC (2014) and Jewell and Wilson (2011), including sample port leak testing procedures to ensure samples are representative of the subsurface. Concentrations of O₂, CO₂, and CH₄ in the soil gas immediately adjacent to the petroleum hydrocarbon-impacted soils can be informative and provide the necessary data to affirm ample influx of atmospheric O₂ and/or CH₄ oxidation. This would affirm site conditions meet the method assumptions (e.g. ample O₂ exchange and complete CH₄ oxidation) and provide information to help with NSZD monitoring design.

At some sites, discontinuous lower permeability or impervious ground cover may non-uniformly affect patterns of CO₂ flux. For a site with a large fraction of low permeability cover, an advanced data objective (e.g. annual NSZD estimate), and higher data quality need (e.g. remedial decision document), then it may make sense to perform a direct-push-type soil gas survey to map the O₂, CO₂, and CH₄ concentrations in the vadose zone. This may be an effective predesign option for sites looking to perform theoretical assessment of NSZD, optimize their networks, and/or minimize the number of NSZD monitoring locations. While concentrations alone are not a good indicator of flux, all else equal and when paired with other LCSM data sets, the information can be used for various purposes, including:

- citing NSZD monitoring locations in zones of low, moderate, and high CO₂ concentration;

- identifying areas containing CH_4 and incomplete CH_4 oxidation; and
- assessing the amount of natural soil respiration that is occurring.

These are two examples amongst many other optional pre-design characterization efforts that could be implemented and be beneficial at some sites in need of an extra level of data for NSZD monitoring program design.

3.1.4 Theoretical Assessment of NSZD

A range of theoretical assessment options can be performed to approximate NSZD rates. They may be useful as a basis for NSZD monitoring program design and/or to establish a benchmark for comparison of field measurements. The assessment output can then be compared to field measurements and used to validate the results. For example, if field measurements are much higher or lower than expected, then additional theoretical scrutiny is advised to evaluate the cause of the discrepancy in the results and potentially adapt the field measurement procedures.

Theoretical assessment of NSZD can be performed using the following options, listed in increasing order of complexity:

- screening-level assessment of NSZD using nomograms,
- analytical calculations,
- modeling.

In general, the simpler the better. Consistent with a theoretical assessment data quality objective and the dynamic spatial and temporal nature of NSZD, the analysis should be performed using a range of measured or assumed values for each input parameter. This will generate a range of plausible NSZD rates which can be useful to refine the LCSM and serve as a benchmark for comparison of field measurements.

3.1.4.1 Using Nomograms to Estimate NSZD Rates

Screening-level NSZD assessment using a nomogram is a useful desktop exercise. Nomograms are drawn using established theoretical analytical equations and a set of known existing or assumed parameters. Because some site-specific parameters may not yet have been measured, they are typically run using a range of values that could be representative of field conditions. Nomograms are also typically graphical in nature, have one axis that is the desired value (i.e. the NSZD rate), and the other axis uses a parameter that is readily available. Inherent to theoretical analysis, they make many simplifying assumptions and as a result, their data quality is considered screening-level.

Figure 3-1 presents a couple example NSZD rate estimate nomograms based on an application of Fick's first law and following the general approach of Davis et al. (2009) (see Equation 4.1). It is important to note that these are not implied to be typical, but rather an example of how a nomogram could be constructed for other site-specific uses. Each project team is advised to construct their own nomograms. The following general assumptions were made to create the nomograms in Figure 3-1.

- A single homogeneous and isotropic layer of clean soil exists above the petroleum hydrocarbon-impacted soils where soil is at equilibrium conditions.
- A hypothetical interface of instantaneous hydrocarbon oxidation exists in this clean soil where the O_2 concentration is zero and oxidation of CH_4 is complete. The O_2 gradient is linear and estimated from atmosphere to the depth of this interface.
- No soil O_2 consumption or CO_2 production occurs due to natural soil respiration.

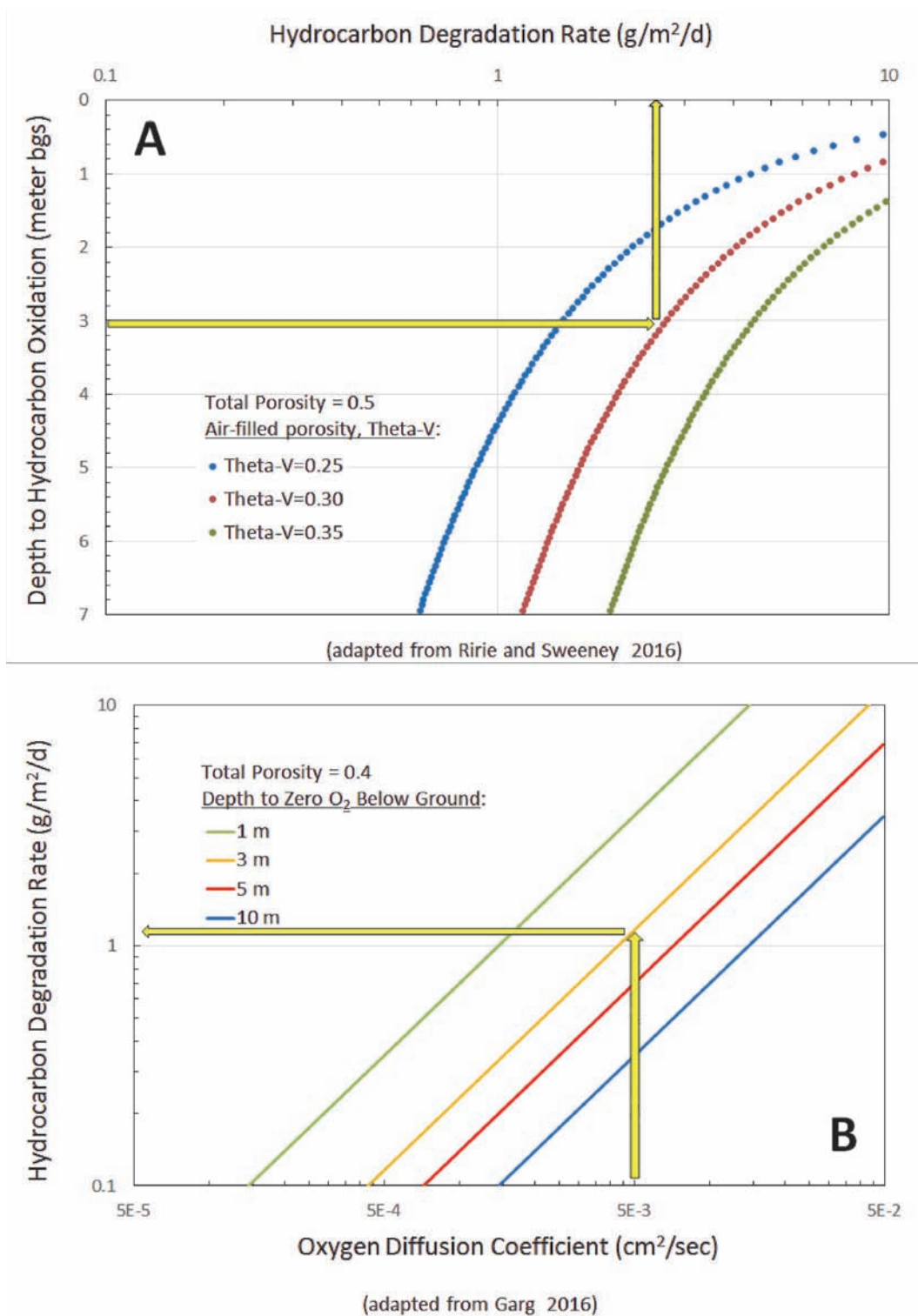


Figure 3-1—Example Use of Nomograms to Estimate NSZD Rates

- The Millington and Quirk (1961) equation can be used to estimate the effective O_2 diffusion coefficient ($D_{O_2}^{eff}$) as shown in Equation 3.1.

$$D_{O_2}^{eff} = D_{O_2}^{air} \times \frac{\Theta_v^{3.3}}{\Theta_T^2} \quad (3.1)$$

where $D_{O_2}^{air}$ is the diffusion coefficient of O_2 in air, Θ_v is the air-filled porosity, and Θ_T is the total porosity of the vadose zone soil within and above the hydrocarbon oxidation zone.

- Heptane (C_7H_{16}) is the representative hydrocarbon with an LNAPL specific gravity of 0.8.

Additional assumptions are stated on the nomograms. With assumptions representative of site conditions, the nomograms in Figures 3-1A and 3-1B can be used to estimate the NSZD rate based on the depth to hydrocarbon oxidation and effective O_2 diffusion coefficient ($D_{O_2}^{eff}$), respectively.

Figure 3-1A indicates that an NSZD rate of 2.2 g/m²/d (1,100 gal/ac/yr) could be expected from a depth to hydrocarbon oxidation of 3 m bgs and an air-filled porosity of 0.3. As explained further in 4.2.2, there are various methods to estimate the depth to hydrocarbon oxidation. For example, it can be approximated using historical borings logs and inferred as the depth interval immediately above hydrocarbon impacted soils.

Figure 3-1B indicates that an NSZD rate of 1.0 to 1.1 g/m²/d (500 to 600 gal/ac/yr) could be expected in soil with a $D_{O_2}^{eff}$ of 0.005 cm²/s and a depth to zero O_2 in soil gas of 3 m bgs. In this nomogram, the depth to zero O_2 in soil gas is being used as a surrogate for the depth to hydrocarbon oxidation. $D_{O_2}^{eff}$ can be estimated using the Millington and Quirk equation (see Equation 3.1) by assuming an air-filled (Θ_v) and total porosity (Θ_T) and $D_{O_2}^{air}$ using a constant of 0.205 cm²/s.

3.1.4.2 Analytical Calculations

A second option for theoretical NSZD assessment that requires slightly more data input and field characterization (e.g. soil gas measurements as discussed in 3.1.3), is the use of more site-specific and detailed analytical equations. Following the general approach of Johnson et al. (2006), the NSZD rate can be estimated using the gradient method without intensive data collection efforts. The data quality, however, will be limited by the validity of the assumptions used in the calculations. The calculations are typically based on key site-specific conditions such as natural soil respiration rates, depth to hydrocarbon oxidation zone, and assignment of the $D_{O_2}^{eff}$ value. The analytical equations can be modified to model multiple lithologic layers.

An example screening-level analytical calculation tool is the vadose zone biological loss model (Wilson et al. 2016b). It is beyond the scope of this document to present the model basis and application of the tool. The tool developers can be contacted for further information.

3.1.4.3 Modeling

A third option for theoretical NSZD assessment that requires far more data input and field characterization is the use of a model. Modeling is reserved only for those with advanced skills, detailed understanding of site conditions appropriate to establish accurate model input, and a clear effort value. Selection of the appropriate model is dependent on the data objectives.

Following the general approach of Sihota and Mayer (2012), the sitewide geospatial and temporal rates of NSZD can also be estimated using a general purpose reactive transport model. An example is the non-commercially available model MIN3P-DUSTY (Molins and Mayer 2007) that was developed for this purpose. It is beyond the scope of this document to present the model basis and application of the tool. The model developers can be contacted for further information.

3.1.5 Method Selection

Three NSZD monitoring methods are currently available and have received widespread use. Selection of which method or methods are appropriate for a particular project and site is a site-specific judgment based on data objectives and site conditions. To assist with method selection, Table 3-3 presents a summary of the methods and their attributes (adapted from Tracy 2015). It is plausible that more than one method may be appropriate for a given project. Regardless, it is important to review the merits and limitations of each method and carefully consider which can best achieve the project goals. The details of each method are described in Sections 4 through 6..

Table 3-3— NSZD Monitoring Method Screening Criteria

	Gradient	Passive Flux Trap	Dynamic Closed Chamber
Best for sites with:	Vadose zones >5 ft (below root zone) with pre-existing vapor sampling probes	Variable effects of natural soil respiration on O ₂ and CO ₂ flux	Uniform background gas flux
Intrusiveness	High, new probe installations (Low if using existing sample probes)	Low, shallow installation	Low, shallow installation
Transport processes quantified	Diffusion	Diffusion, advection ^a	Diffusion, advection ^a
Instantaneous or time-averaged measurement?	Instantaneous	Time-averaged	Instantaneous or time-averaged
Method of background (i.e. non-NSZD related processes) correction	Background O ₂ and/or CO ₂ flux monitoring ^c	¹⁴ C	Background CO ₂ efflux monitoring ^c
Spatial coverage/data density	Low	Moderate	High
Real-time data	Yes, using field gas analyzer	No	Yes
Laboratory analysis	Optional	Yes	No
Field labor intensity	High	Low	Moderate
Relative one-time implementation cost ^b	\$\$\$ (\$-\$\$ if using existing sample probes and field gas analyzer)	\$\$	\$
^a Methods quantify the combined effects of diffusion and advection. The method does not allow for the quantification of the individual contributions from each gas transport process, however. ^b Reported cost ranges include an accounting of the labor, materials, and analytical expenses required to perform a one-time round of NSZD measurements. For the gradient method, it is inclusive of costs for soil gas sampling probe installation, D ^{eff} _v tests, and field measurement of soil gas profiles using nested vapor probes. For the passive flux trap method, it is inclusive of trap supply, lab analysis of CO ₂ and ¹⁴ C, and field installation and retrieval. For the DCC method, it is inclusive of DCC unit rental, collar installation and retrieval, and one round of field measurements. ^c New methods of using ¹⁴ C correction on soil vapor samples are emerging. See 7.3 for more details.			

3.1.6 Correcting Gas Flux Measurements for Non-NSZD Processes

Estimating NSZD-related fluxes is complicated by natural soil respiration (Rochette et al. 1999). In this document, “background” is considered O₂ utilization, CO₂ production, and/or CH₄ production or oxidation that is unrelated to the presence of the petroleum hydrocarbon LNAPL source. This includes contributions from plant roots and microbes present in surficial soils and deeper soils containing natural organic matter such as peat as humic matter. These processes tend to be most significant in the root zone and diminish with increasing depth, but are variable from site to site and remain a subject of ongoing research (see 8.2).

Potential strategies to account for the contribution of background soil respiration to O₂ or CO₂ fluxes, from simple to more complex, include:

- background gas flux monitoring outside the LNAPL footprint;
- supplementing with a second measurement method (i.e. passive flux trap with ¹⁴C correction) to estimate the background gas flux; and/or
- measuring ¹⁴C in soil vapor to identify the contribution of CO₂ originating from petroleum vs non-petroleum sources (Sihota and Mayer 2012; Sihota et al. 2016).

There are numerous challenges with background correction using results from outside the LNAPL footprint, especially at sites with diverse ground cover, very active natural soil processes, or deep LNAPL source zones. More complex site conditions will drive selection of a more complex background correction process.

One strategy to eliminate flux contributions from non-NSZD processes is to install gas flux measurement locations in a nearby uncontaminated setting with similar surface and subsurface conditions. Estimate fluxes for these background locations in the same way as used for the locations overlying the LNAPL footprint. Subtract the background flux from the total flux measured atop the source zone to estimate the NSZD rate. The number of background locations will be driven by the variability in the background flux results. If large variability is observed, then a statistical approach may be useful (e.g. based on pre-established confidence limits).

Figure 3-2 shows the hypothetical placement of CO₂ efflux DCC survey locations at a site with an LNAPL body across two different surface soil conditions. Calculation of CO₂ efflux from petroleum hydrocarbon sources (JNSZD) is given by Equation 3.2, where J_{Total} is the total uncorrected CO₂ efflux from each survey location atop the LNAPL footprint and J_{Background} is the average CO₂ efflux measured at the background locations in each different ground cover:

$$J_{NSZD} = J_{Total} - J_{Background} \quad (3.2)$$

As shown in Figure 3-2, the BG1 and BG2 survey locations would be used to correct the total CO₂ efflux measured at survey locations within ground cover Type 1. Similarly, the BG3 and BG4 survey location would be used to correct the total CO₂ efflux measured at survey locations within ground cover Type 2. The use of ¹⁴C provides an alternative more accurate means to isolate the NSZD-derived CO₂ flux without the need to monitor areas outside of the LNAPL footprint. This can be especially relevant to sites with variable ground cover and soil conditions which affect background CO₂ and O₂ flux. Therefore, it is important to determine which method of background correction will be used as part of the NSZD program design stage because it will affect the number of locations to be measured. More detailed discussion of the ¹⁴C background corrections methods are provided in 5.4.2 (for the passive flux trap) and 7.3 (an emerging method).

3.1.7 Monitoring Frequency

The number and frequency of gas flux monitoring events at a site depends on various factors including data objectives (see 3.1.2), climatic conditions, and whether the site exhibits a fluctuating groundwater table. Sites with seasonal fluctuations in the groundwater table which intermittently expose and submerge the LNAPL should have at least two measurements completed: one during high water table periods and the other during a low water table period. The effects of seasonality on CO₂ efflux from the ground surface can also be assessed with multiple monitoring events at a site throughout the year. Examples of seasonal effects include varying levels of soil moisture throughout the year, temperature (including frozen ground), and humidity changes (Sihota et al. 2016).

3.2 Gas Flux Monitoring Field Implementation

An NSZD monitoring program contains various implementation elements important for success. They are described in detail in this section.

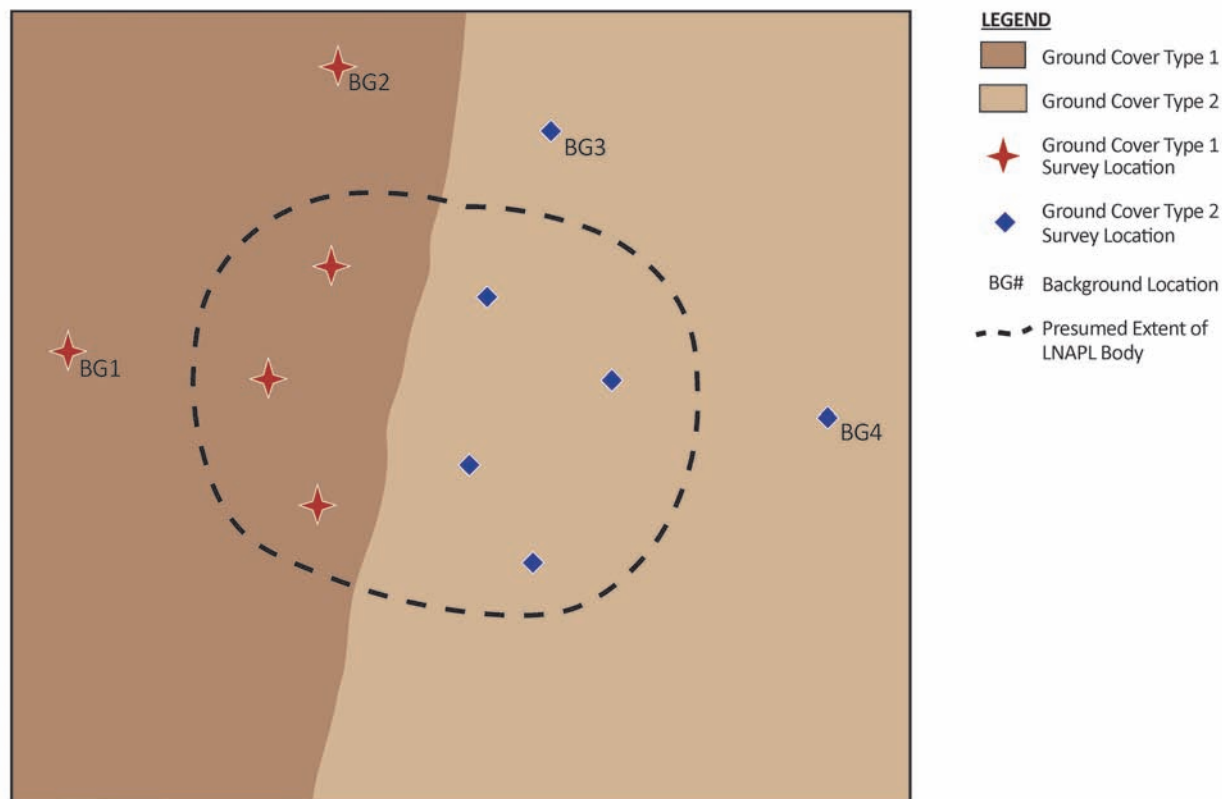


Figure 3-2—Example Placement of Survey Locations for DCC Method

3.2.1 Ambient Monitoring

NSZD rates from soil gas flux monitoring methods are affected by subsurface conditions including soil temperature and moisture content. Therefore, it is typically prudent to monitor ambient air conditions and precipitation during implementation of the NSZD monitoring program. Daily measurements of maximum and minimum ambient air temperature and rainfall/snowfall can be useful to support data evaluation. For example, warmer ambient temperatures may increase vegetation-related CO₂ production and cause higher-biased total efflux measurements. Rainfall increases the soil moisture and can also significantly affect flux measurements by temporarily altering vapor diffusivity.

Other atmospheric conditions to monitor include wind speed and large changes in barometric pressure.

It is often useful to have these site condition records to facilitate understanding of the measurements during data evaluation after field demobilization. These measurements can be collected using a site-specific weather monitor or a local weather station such as a permanent unit that may be present at the nearest airport.

3.2.2 Ground Cover and Surface Soil Characterization

When using the DCC or passive flux trap methods it is important to characterize and carefully scrutinize the ground cover upon which the measurements are made. Both methods are susceptible to interference from ground surface or shallow subsurface anomalies such as rain water pools or utility trenches. Therefore, in order to avoid collecting erroneous, non-representative data, it is important to avoid installation in these types of areas. Typically, a visual survey can quickly and effectively identify evidence of these anomalies.

Vegetation should also be closely inspected across the footprint of the NSZD CO₂ efflux surveys using the passive flux trap and DCC methods. Where ¹⁴C analysis is not used, background CO₂ efflux related to root zone respiration must be characterized because of the potentially large contribution from root zone respiration and the associated challenges with correcting for it. Where CO₂ efflux methods are preferred and ground cover is either highly variable or thick in vegetation, CO₂ traps with ¹⁴C analysis is recommended to most accurately estimate NSZD. Emerging methods to use ¹⁴C to correct results from the gradient and DCC methods are also discussed in 7.3. Photo documentation of each survey location can be particularly helpful in assessment of parsed data sets after field demobilization.

Surface soil conditions should also be logged to identify soil types (i.e. coarse or fine-grained, organic matter content, moisture content, and soil density). These soil properties can also support installation and data evaluation needs. For example, ground cover anomalies can be identified and avoided. Areas of compacted soil can also be identified and avoided or installation methods adapted to avoid puncturing compacted layers and creating “chimneys” of high CO₂ efflux.

3.2.3 Installation Procedures

Systematic installation methods, such as those included in Appendix A, are important to the success of an NSZD monitoring program. Comparable data are created when uniform installation methods are used to scribe, install, and re-compact soils around and inside the DCC and passive flux trap units. Systematic procedures are similarly important for the vapor monitoring probes associated with the gradient method.

Of particular note, re-compaction of soils is no simple task and must be performed carefully to return soils around and inside the DCC collars and traps to as close to pre-existing conditions as possible. Anomalous results can occur when installation is not consistent; false high CO₂ efflux can occur when soil is not compacted enough and false low CO₂ efflux results can occur when it over-compacted. One procedure that has been successfully deployed is to use a manual compaction slide hammer with a 12 in. drop weighing 5.5 lbs. The slide hammer is dropped one to three times depending on initial ground cover density to recompact soil to as close to original conditions as possible. Using standard re-compaction procedures for DCC collar or trap installation minimizes the chances of outside infiltration of air and also increases the likelihood that each unit is installed in a very similar fashion such that the measured efflux is representative and comparable. As discussed in the following section, field duplicates can help ascertain the consistency of installations.

3.2.4 Quality Assurance and Quality Control

In addition to the manufacturer's recommended instrument calibration, the following QA/QC procedures are recommended to facilitate NSZD data quality assessment.

- Field blank: relevant to the DCC method, the chamber is placed on an air-tight collar and allowed to collect a series of blank measurements. An example field blank measurement procedure is prescribed in Appendix A.
- Trip blank: relevant to the passive flux trap method, a laboratory-sealed trip blank trap accompanies the shipment from point of origin through field deployment and back to laboratory. Results are used to measure the incidental amount of CO₂ sorbed by the trap during manufacturing and transport. The CO₂ collected by the trip blank is subtracted from all other traps to correct the final results.
- Duplicate: relevant to all methods, used to assess reproducibility of measurements in side by side installations.

The results of the QA/QC samples can be used to perform a data quality evaluation, similar to that done for groundwater analytical chemistry. Detection limits can be assigned, results adjusted for cross contamination, and data can be qualified due to poor duplicate correlation in the field.

3.3 Data Evaluation

An NSZD monitoring program contains various data evaluation elements important for success. They are described in detail in this section.

3.3.1 Units of Measurement

The units most commonly involved in NSZD measurements are summarized on Table 3-4. Selection of reporting units is a site-specific judgment, but should be carefully selected to be consistent with the spatial and temporal nature of the measurement and, if used for remedial technology comparison purposes, units used to report the effectiveness of other remedial technologies at the site.

Table 3-4—Units of NSZD Measurement

Parameter	International System (SI) Units		Imperial Units	
	Unit	Abbrev.	Unit	Abbrev.
Gradient Method	milligrams/square meter/hour or grams/square meter/second	mg/m ² /hr or g/m ² /s	Not commonly used	
Gas Flux	micromoles/square meter/second	μmol/m ² /s	Not commonly used	
Mass-based NSZD Rate	grams/square meter/day	g/m ² /d	pounds/square ft/day	lb/ft ² /d
	kilograms/square meter/year ^a	kg/m ² /yr	pounds/square foot/year	lbs/ft ² /yr
Volumetric NSZD Rate	liters/square meter/day	L/m ² /d	gallons/square foot/day	gal/ft ² /d
	cubic meters/square meter/year ^a	m ³ /m ² /yr	gallons/acre/year ^c	gal/ac/yr ^c
Sitewide Mass-based NSZD Rate ^b	kilograms/day	kg/d	pounds/day	lb/d
	kilograms/year ^a	kg/yr	pounds/year	lb/yr
Sitewide Volumetric NSZD Rate ^b	liters/day	L/d	gallons/day	gal/d
	cubic meters/year ^a	m ³ /yr	gallons/year	gal/yr
^a Annual NSZD rates should be based on multiple temporal measurement events and assessment of seasonality as discussed in 3.3.4. ^b Sitewide NSZD rates should be based on multiple geospatial measurements and assessment of geospatial variability as discussed in 3.3.3. ^c The units of gallons/acre/year (gal/ac/yr) is a common reporting unit for passive CO ₂ flux traps. This unit may be appropriate, but should be supported by a geospatial and temporal variability assessment as discussed in both 3.3.3 and 3.3.4.				

3.3.2 Stoichiometry to Estimate NSZD Rate from CO₂ and O₂ Flux

An NSZD rate can be calculated at each gas flux measurement location by Equation 3.3:

$$R_{NSZD} = \left[\frac{J_{NSZD} m_r MW}{10^6} \right] \times \frac{86400s}{d} \quad (3.3)$$

where R_{NSZD} is the total hydrocarbon degraded (g/m²/d), J_{NSZD} is the background corrected soil CO₂ flux (μmol/m²/s), m_r is the molar ratio of hydrocarbon degraded per CO₂ produced or O₂ consumed in mineralization reaction (unitless), and MW is the molecular weight of the representative hydrocarbon (g/mol).

To make the stoichiometric conversion from a mass-based NSZD rate to volume-based rate, two key properties of the LNAPL source zone are required:

- predominant hydrocarbon,
- LNAPL density.

A review of chromatograms from soil total petroleum hydrocarbon analysis or LNAPL samples can be used to select the predominant hydrocarbon remaining in the LNAPL. After isolation of the predominant carbon number compound, a common constituent (e.g. heptane, octane, or dodecane) can be chosen and used to tailor the stoichiometric conversions. To demonstrate, octane was chosen as a representative hydrocarbon due to the predominant presence of lighter end hydrocarbons in the example LNAPL. The mineralization of octane is represented by Equation 3.4:



In this example, to estimate the mass of octane degraded, the CO_2 flux would be multiplied by the molar ratio of octane to CO_2 (2/16) and multiplied again by the molar weight of octane (114.23 g/mol). Table 3-5 lists example representative hydrocarbons, stoichiometric equations, and multiplication factors for a range of light-to heavy-end hydrocarbons and conversion of CO_2 flux to NSZD rates.

Table 3-5—Example Representative Hydrocarbons and CO_2 Flux Stoichiometric Conversion Factors

Representative Hydrocarbon	Chemical Formula	Stoichiometric Equation	Molecular Weight of HC	Stoichiometric Ratio HC: CO_2	CO_2 Flux Multiplier
Benzene	C_6H_6	$2 \text{C}_6\text{H}_6 + 15 \text{O}_2 \rightarrow 12 \text{CO}_2 + 6 \text{H}_2\text{O}$	78.1	0.16	13.0
Heptane	C_7H_{16}	$\text{C}_7\text{H}_{16} + 11 \text{O}_2 \rightarrow 7 \text{CO}_2 + 8 \text{H}_2\text{O}$	100.2	0.14	14.3
Octane	C_8H_{18}	$2 \text{C}_8\text{H}_{18} + 25 \text{O}_2 \rightarrow 16 \text{CO}_2 + 18 \text{H}_2\text{O}$	114.2	0.125	14.3
Decane	$\text{C}_{10}\text{H}_{22}$	$2 \text{C}_{10}\text{H}_{22} + 33 \text{O}_2 \rightarrow 20 \text{CO}_2 + 22 \text{H}_2\text{O}$	142.3	0.10	14.2
Dodecane	$\text{C}_{12}\text{H}_{26}$	$2 \text{C}_{12}\text{H}_{26} + 37 \text{O}_2 \rightarrow 24 \text{CO}_2 + 26 \text{H}_2\text{O}$	170.3	0.083	14.2
Tetradecane	$\text{C}_{14}\text{H}_{30}$	$2 \text{C}_{14}\text{H}_{30} + 43 \text{O}_2 \rightarrow 28 \text{CO}_2 + 30 \text{H}_2\text{O}$	198.4	0.071	14.2
NOTE HC = hydrocarbon					

It should be noted that although the stoichiometric equations may look different using various representative hydrocarbon compounds, biologically mediated petroleum hydrocarbon oxidation tends to use similar stoichiometric ratios of O_2 and CO_2 . Therefore, the hydrocarbon selection is relatively insensitive to the stoichiometric conversion and estimation of the NSZD rate from gas flux. As shown on Table 3-5, the difference in CO_2 flux multipliers across all example hydrocarbons is less than 10 %.

Either a site-specific fluid properties analysis or a reasonably approximated value from published literature can be used to estimate the LNAPL density (API 2016). The LNAPL density (ρ) is used to convert the mass-based NSZD results ($R_{\text{NSZD-mass}}$) to volume-based results ($R_{\text{NSZD-vol}}$) that tend to be more comprehensible in a site remediation context. Equation 3.5 shows how this calculation can be made.

$$R_{\text{NSZD-vol}} = \frac{R_{\text{NSZD-mass}}}{\rho} \quad (3.5)$$

Using mixed SI and Imperial units (which is common), Equation 3.6 shows conversion of mass- ($R_{\text{NSZD-mass}}$ in $\text{g/m}^2/\text{d}$) to volume-based ($R_{\text{NSZD-vol}}$ in gal/ac/yr) NSZD results using the LNAPL density (ρ in g/cm^3) as follows:

$$R_{\text{NSZD-vol}} = \frac{R_{\text{NSZD-mass}} \times 264.17 \frac{\text{gal}}{\text{m}^3} \times 4046.86 \frac{\text{m}^2}{\text{ac}} \times 365 \frac{\text{d}}{\text{yr}}}{\rho \times 10^6 \frac{\text{cm}^3}{\text{m}^3}} \quad (3.6)$$

3.3.3 Estimating Site-wide NSZD Rates

If the data use (see 1.6) and data objective (see 3.1.2) drive the need and enough representative measurements are made across the lateral extent of the LNAPL footprint, then a site-wide estimate of NSZD can be made. Stated simply, a site-wide NSZD rate (in units of mass per time, e.g. lb/d) can be estimated by multiplying a unit loss rate (e.g. lb/ac/d) by an estimated lateral area of the LNAPL source zone (e.g. ac). If unit rates have been estimated at multiple locations, each can be apportioned to a representative area using geospatial tools.

Various geospatial analysis tools are available to perform these calculations ranging from simple manual contouring, to Thiessen polygons, to more intensive geographic information system (GIS)-based contouring and integration (U.S. Army Corps of Engineers 1997 and US EPA 2004). Figure 3-3 presents a conceptual depiction of a contouring graphic used to estimate a site-wide NSZD rate. In this example, the method used to obtain a simple, area-integrated NSZD rate for the entire site, included using linear interpolation to contour the individual NSZD rates at all survey/monitoring locations and using commercial software means to estimate the areas within each contour interval. The areas within each isoconcentration level were then multiplied by the average NSZD rate within each contour interval. All of the rate-area values were then summed to estimate a total or site-wide NSZD rate.

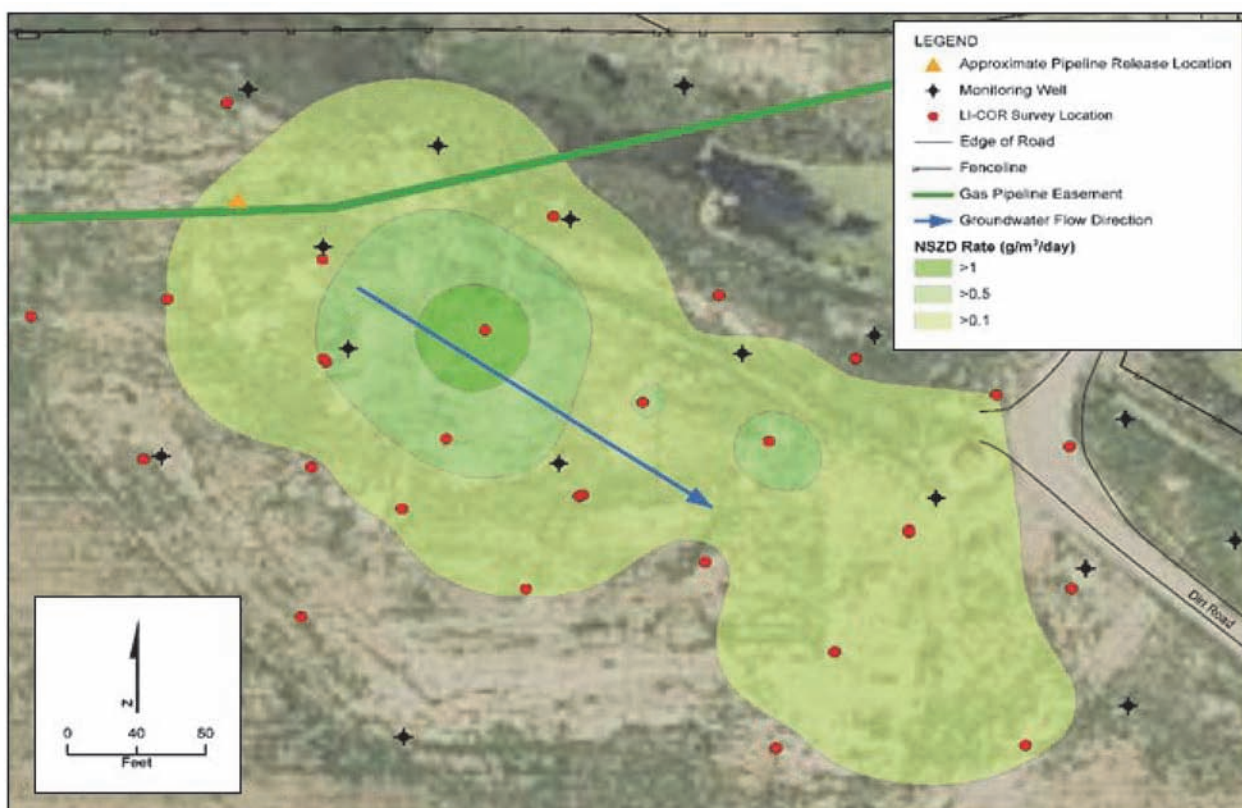


Figure 3-3—Example Conceptual Depiction of Site-wide NSZD Rate Contouring

A couple notes of caution on estimating site-wide NSZD rates using geospatial interpolation: Parallel to the heterogeneity of hydrocarbon impacts in soil, NSZD rates vary geospatially and this variability must be adequately captured with the NSZD monitoring program prior to geospatial interpolation (Sihota et al. 2011). Additionally, the timespan of the estimate is limited to the duration of the measurement events. Typically, measurements taken using either of the three methods discussed herein are limited to use in estimating a daily rate of NSZD. If annual rates of NSZD are desired, then additional measurements are required as discussed in the next section. Finally, the complexity of site conditions such as the number of hydrocarbon release areas and presence of discontinuous low-permeability ground cover or shallow soil, may preclude the use of geospatial interpolation or at a minimum demand use of a more robust procedure using statistical confidence limits. The practitioner is advised to carefully consider the data objectives, data quality, and site conditions and provide statistical caveats on the results so that the data use remains within appropriate limits.

3.3.4 Estimating Annual NSZD Rates

If the data use (see 1.6) and data objective drive the need (see 3.1.2) and enough site-wide NSZD measurements are collected over time to account for seasonal variability, then an annually extrapolated NSZD rate (lb/yr or gal/yr) can be made. This can be done after information is gathered to adequately understand the seasonal changes on subsurface NSZD rates. Seasonal changes are primarily temperature- and moisture-related (Sihota et al. 2016).

A couple notes of caution on estimating annual NSZD rates. For the aforementioned reasons, NSZD rates can vary with time and this variability must be adequately captured with the NSZD monitoring program. For the Bemidji site in Minnesota, Sihota et al. (2016) found that NSZD rates in the summer were 60 % larger than the average annual NSZD rate estimated from periodic DCC measurements. The timespan of the individual, short-term NSZD estimates is limited to the duration of the measurement events, typically daily. These one-time estimates should not be extrapolated in time unless subsurface conditions are observed to be monotonic.

It is also important to note that NSZD rates are expected to decline as LNAPL source mass is depleted over the multiple decades of time that it will persist in the subsurface (Revesz et al. 1995). However, there is currently no published literature that documents changes in NSZD rates over long periods (i.e. greater than 20 years). In the absence of this research, the current assumption is that NSZD rates are zero order (i.e. the same rate year over year) for the majority of the time that LNAPL persists in the subsurface. The practitioner is advised to keep abreast of current research on this important topic (see 8.2).

4 Gradient Method

The gradient method uses soil gas measurements of NSZD reaction gases taken at discrete depths to estimate their fluxes through the vadose zone. The reaction gas fluxes are then stoichiometrically equated to an NSZD rate. The gradient method first emerged for use in measuring soil gas flux in the 1970s (Maier and Schack-Kirchner 2014). In the past decade, new sensors and measurement devices have enabled and stimulated its use. For example, Tang et al. (2005) combined continuous soil CO₂ efflux estimates derived using the gradient method to cover temporal variability of the soil gas flux and periodic chamber measurements to cover the spatial variability. These studies demonstrated the gradient method's potential as a suitable tool for both short- and long-term studies. As a consequence, the method has gained increased attention. The gradient method was first applied to estimate NSZD in 2006 (Johnson et al. 2006; Lundegard and Johnson 2006).

4.1 Method Description

The gradient method is a one-dimensional application of Fick's first law (Fick 1855), which states that a chemical will diffuse from a region of high concentration to a region of low concentration:

$$J = D_v^{eff} \left(\frac{dC}{dz} \right) \quad (4.1)$$

The steady-state diffusive flux, J , is proportional to the concentration gradient dC/dz . The constant of proportionality is the effective vapor diffusion coefficient, D_v^{eff} (note that this term is also known as the effective diffusivity).