

Quantification of Vapor Phase-related Natural Source Zone Depletion Processes

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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.

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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.

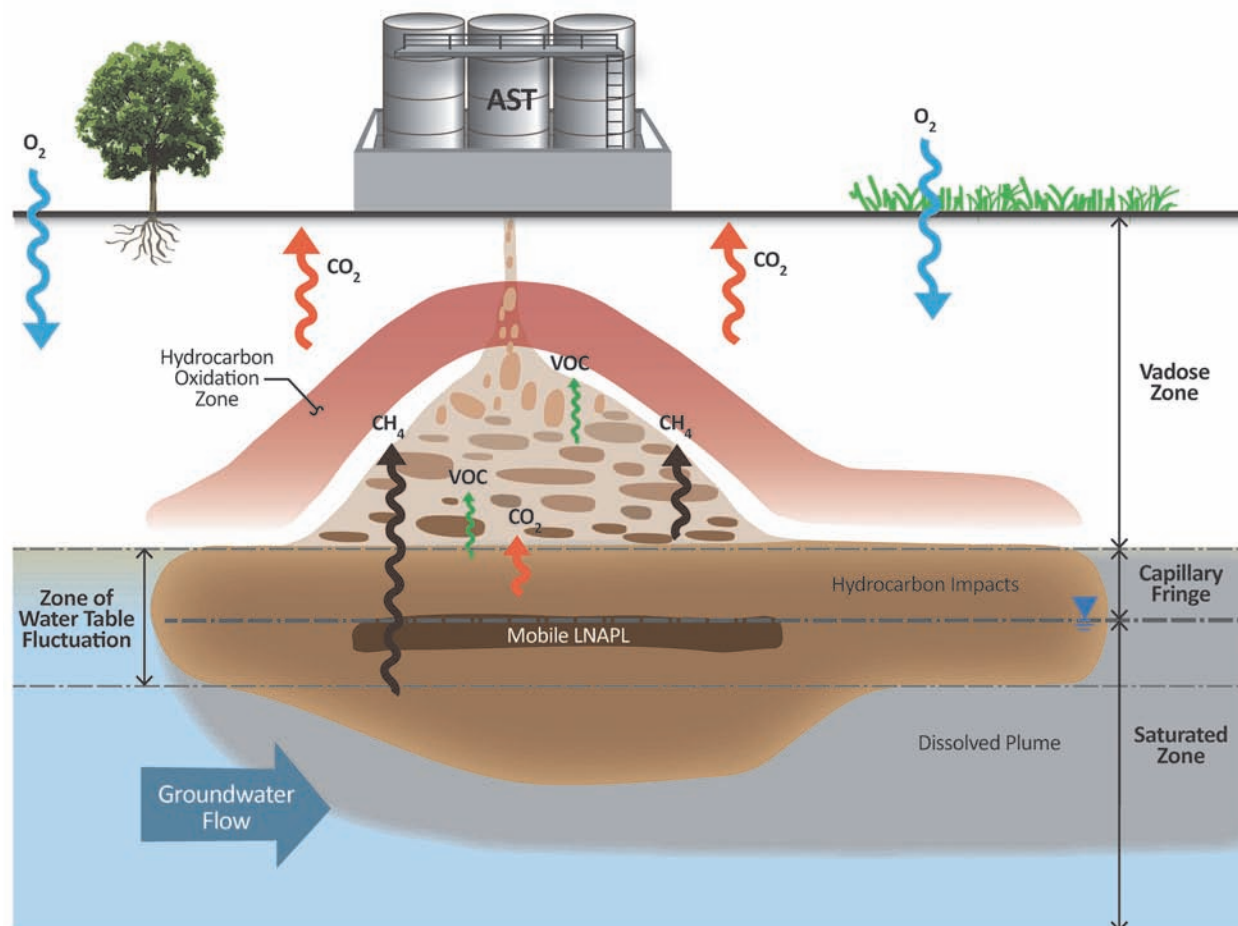


Figure 1-1
Conceptualization of Vapor Phase-Related NSZD
Processes at a Petroleum Release Site

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.

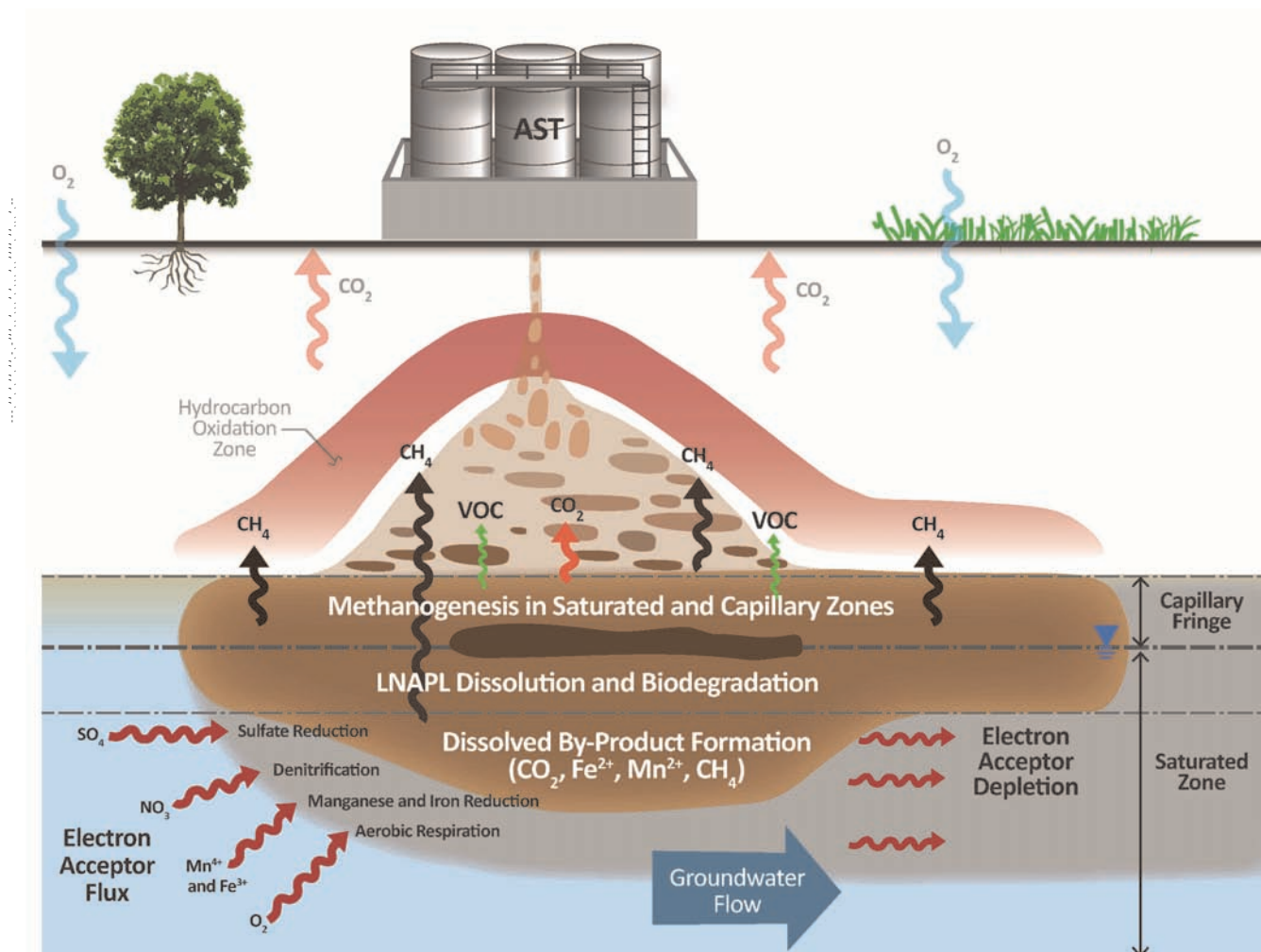


Figure 2-1—Conceptualization of Saturated Zone NSZD Processes

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.

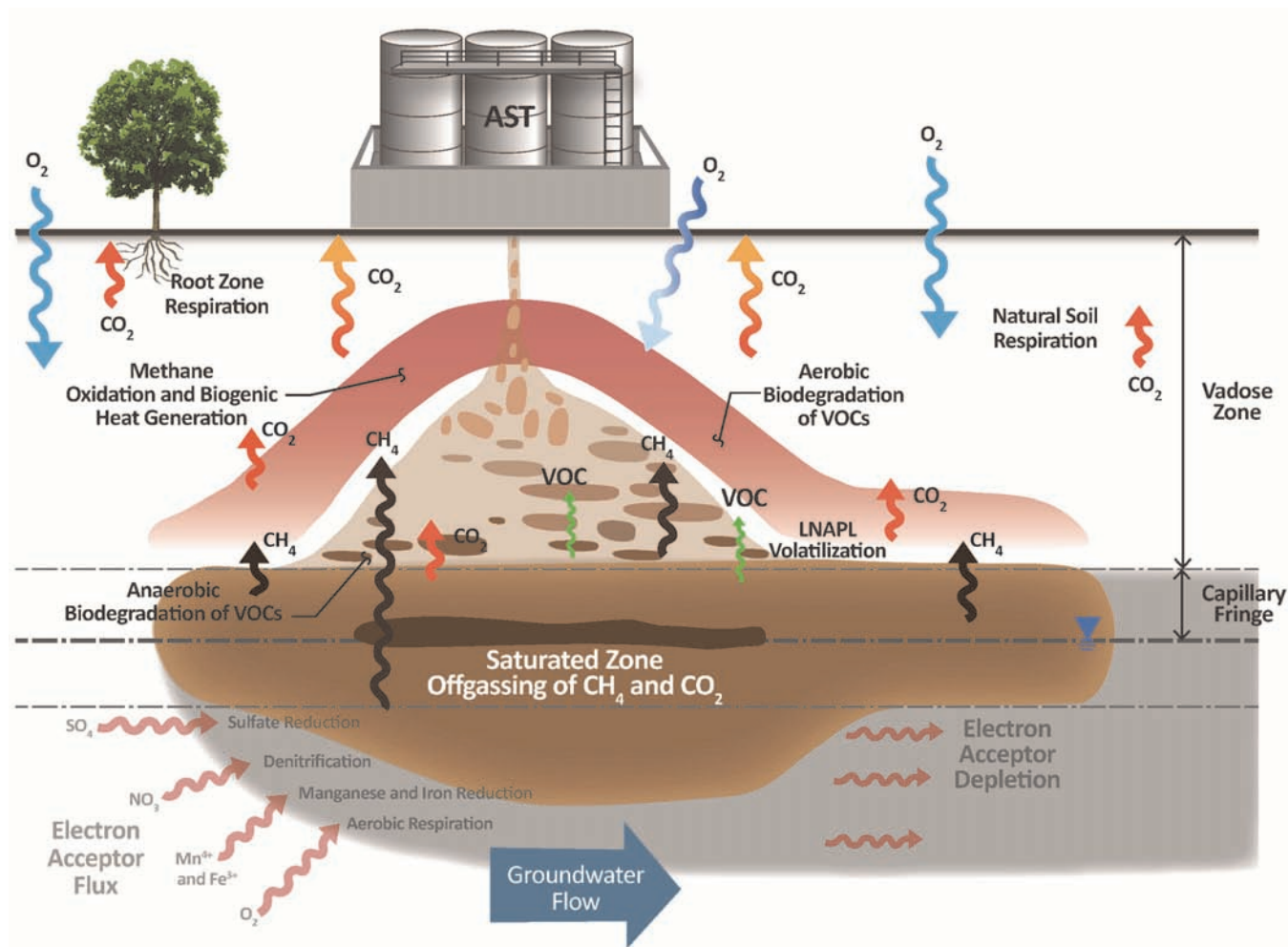


Figure 2-2—Conceptualization of Vapor Phase-related NSZD Processes

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 ($D_{\text{eff},v}$) 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).

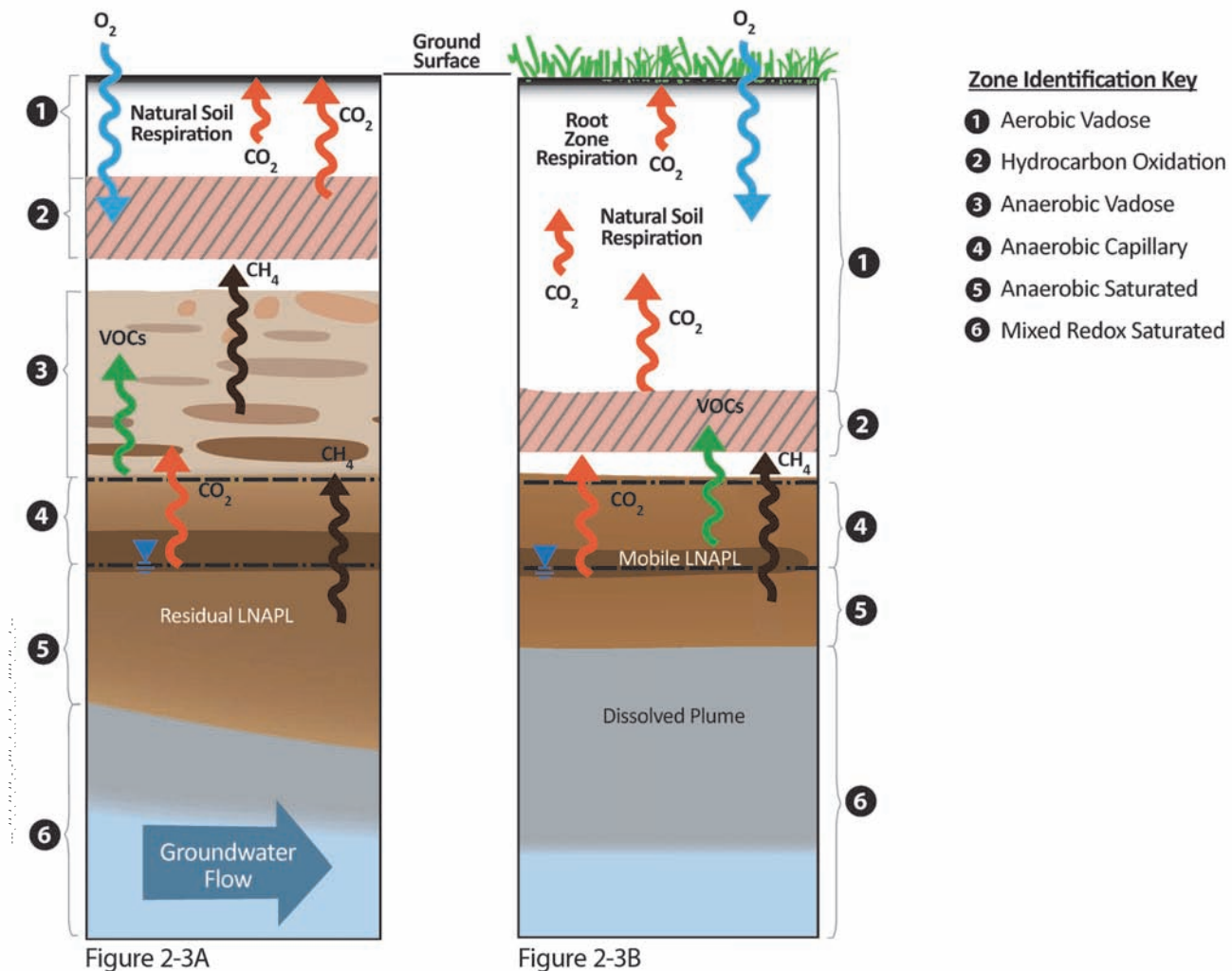


Figure 2-3—Conceptualization of Vapor Phase-related NSZD Processes (a) with and (b) without Hydrocarbon Impacts in the Vadose Zone

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 O₂ is transported downward and the efflux of CO₂ from subsurface NSZD processes is mixed with CO₂ that is created by decomposition of natural organic matter in the soil and root zone respiration. The amount of CO₂ 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 CO₂ 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 O₂ meets upward migrating CH₄ and VOCs and creates an oxidation reaction where the hydrocarbons are converted to CO₂ and heat. This zone may contain hydrocarbon-impacted soils; if it does, then a zone of aerobic petroleum biodegradation is present which creates more CO₂. The rate of CH₄ oxidation is limited by the rate of O₂ 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 effects 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.

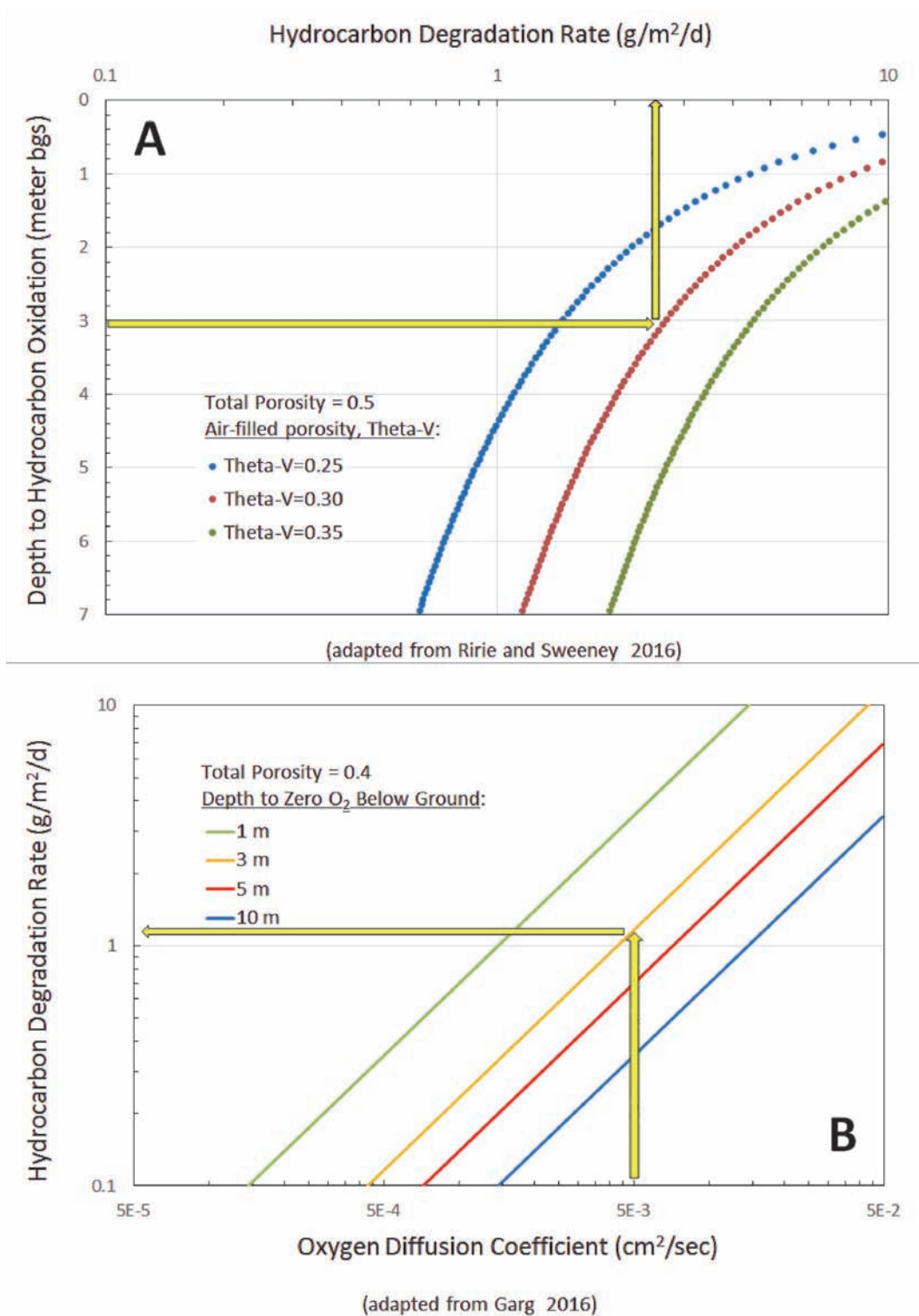


Figure 3-1—Example Use of Nomograms to Estimate NSZD Rates

- 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_v^{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.

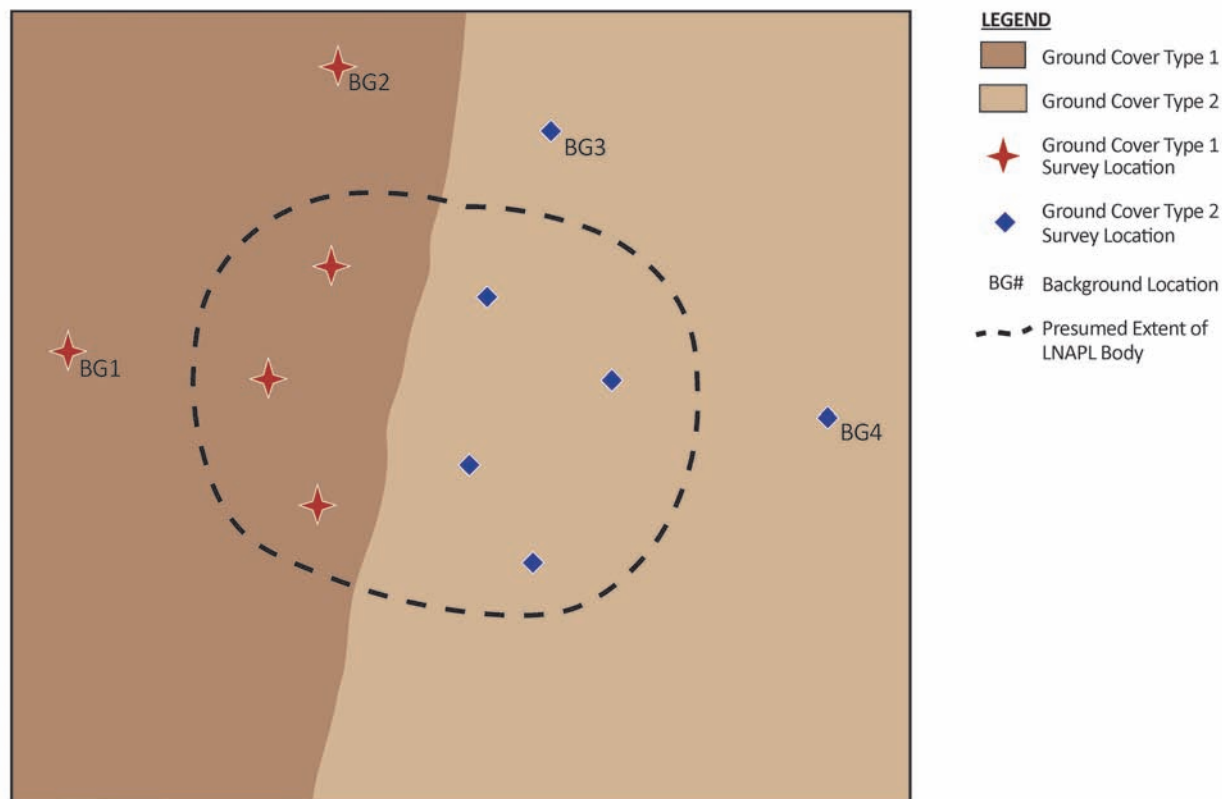


Figure 3-2—Example Placement of Survey Locations for DCC Method

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.

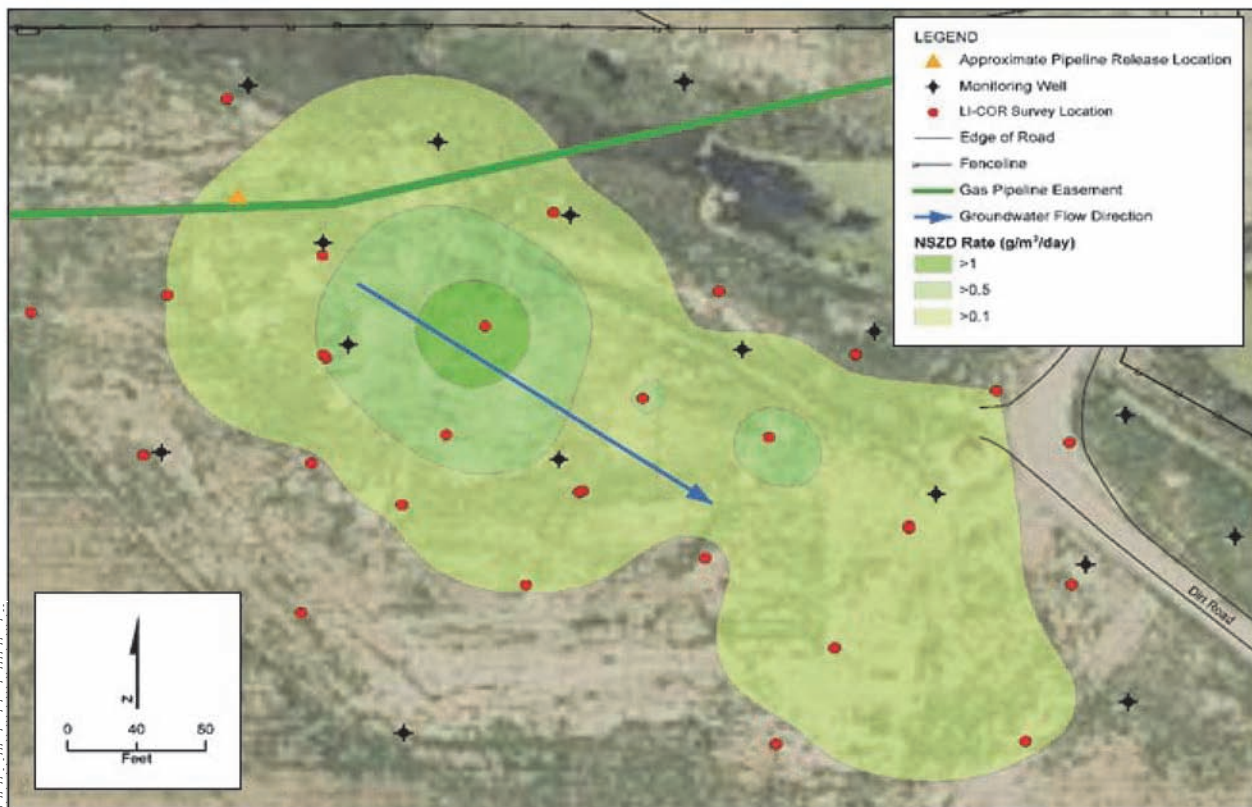


Figure 3-3—Example Conceptual Depiction of Site-wide NSZD Rate Contouring

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).

It is useful to think of the gradient method as analogous to estimating a groundwater flow rate using Darcy's law. Darcy's law states that advective flux is proportional to the hydraulic gradient, where the constant of proportionality is the hydraulic conductivity. Because both Fick's and Darcy's laws rely on estimating a gradient and a parameter that depends on the soil and fluid or chemical of interest, applications of both laws share similar levels of accuracy and uncertainty.

Application of the gradient method is founded on the following two key assumptions.

- Diffusion is the dominant process for gas flux (i.e. no significant advective transport—this will be true in most cases as discussed in 2.1.2).
- Vadose zone soil is homogeneous and isotropic and can be represented by a single representative D_{eff_v} .

NSZD rates can be estimated based on gradient method calculation of the downward O_2 influx or the upward CO_2 flux. They are virtually equivalent measures if all hydrocarbon and methane vapors are oxidized before reaching the land surface (Lundegard and Johnson 2006). Thus, the calculated O_2 influx can serve as a check on the calculated CO_2 flux, or vice versa. Additionally, as discussed further in 7.2, the gradient method can be used to estimate the CH_4 flux, if shallow CH_4 is present at the site.

Application of the gradient method consists of the following steps.

- a) Installing the multi-level vapor sampling probes.
- b) Performing diffusivity testing to measure D_{eff_v} (must be conducted simultaneously with soil gas concentration measurements).
- c) Sampling soil vapor from the monitoring probes and measuring O_2 , CO_2 , CH_4 , and VOC concentrations.
- d) Estimating the concentration gradient.
- e) Assessing and compensating for background fluxes.
- f) Calculating the gas flux.
- g) Converting gas flux to a hydrocarbon mass loss (NSZD) rate.

Each of these steps is described in detail below.

4.2 Program Design Considerations

In addition to the common program design considerations discussed in 3.1, a number of additional factors are considered when designing a gas flux survey using the gradient method.

4.2.1 Installing the Monitoring Probes

Probes for NSZD monitoring are typical of those used in routine soil gas monitoring. The probe points are typically of discrete size, approximately 6 to 12 in. length and less than 1 in. diameter, and connected to smaller diameter tubing run to ground surface. The probe points should be installed with an overlying hydrated bentonite seal to mitigate atmospheric short-circuiting. API (2005) includes detailed recommendations on the installation of temporary and permanent soil vapor probes. The US EPA has developed a standard operating procedure for soil gas sampling, including constructing and installing sampling probes (US EPA 2001). Additional details on probe installation and active gas sampling procedures can be found in CalEPA 2012.

4.2.1.1 Location Selection and Data Density

The spatial coverage achievable using the gradient method can be limited because it typically uses depth-discrete multi-level soil gas probes. A dedicated system can be costly to install and sample and depends significantly upon depth, drilling method, and material selection. Where possible, it is preferred to use existing equipment or install the probes as multi-purpose (e.g. use for NSZD and remedial performance monitoring). A typical installation may have only one to five multi-level probe locations across the LNAPL footprint. Thus, the careful selection of horizontal and vertical sampling locations is critical to gather a representative data set.

4.2.1.2 Horizontal Probe Positioning

Ideally, soil gas probes are located over the LNAPL footprint. As discussed in 3.1, use the LCSM and all available lines of evidence to choose appropriate locations for nested soil gas probes. Position them over the petroleum hydrocarbon-impacted soils, but not near release location(s). Locating probes near a release (i.e. a vertically continuous interval of soil impacts) increases the potential to overestimate NSZD. NSZD rates would be high-biased from gas flux contributions from shallow biodegradation of hydrocarbons. This, in turn, would generate a result that is not representative of the LNAPL footprint, the vast majority of which contains petroleum hydrocarbon-impacted soils only within the saturated zone interval.

4.2.1.3 Vertical Probe Positioning

In choosing depths for soil gas probes, the overall objective is to resolve the concentration gradient in sufficient detail to obtain a representative NSZD rate estimate. Consider two typical site condition scenarios: (A) petroleum hydrocarbon impacts in the vadose zone soil and no surface vegetation and (B) LNAPL in the capillary fringe and a clean overlying vadose zone (i.e. no hydrocarbon impacted soil) and near surface vegetation and a root zone. Figure 4-1 depicts example soil gas sample port installations for the gradient method for both site condition scenarios. Note that the identified zones are the same as described in 2.1.3. For example, Zone 2 is intended to denote the hydrocarbon oxidation zone where the largest reaction of atmospheric O_2 and subsurface CH_4 occurs.

In practice, subsurface gas concentrations are vertically variable. Moreover, important features controlling gas migration in the subsurface may be unknown prior to probe installation. Thus, a good strategy is to perform pre-design characterization including sampling soil gas from existing monitoring wells partially screened in the vadose zone as described in 3.1.3 and/or install multiple probes at different depths. Below is general guidance on probe installation, given a priority, from “need to have”.

- **Need to have:** At least one sampling probe in the preferred depth range shown on Figure 4-2. If the depth of the hydrocarbon oxidation zone is unbounded by existing data, then it is better to position a probe too deep than too shallow. In practice, the target depth for the deepest probe would often be near the top of the hydrocarbon impacted soil (Zones 3 and 4). Consider all available lines of evidence to assess the suitability of the deepest soil gas sample location. In practice, it may take installation of more than one probe in the suspected preferred region to find the “right” location.
- **Nice to have:** Intermediate sample probes positioned between the ground surface and the deepest probe(s). Each additional probe may add useful information, revealing variations in gradient with depth. While sample results from these probes may help refine the LCSM, diminishing returns are inevitable because much of the data may not be used for the NSZD rate calculations. Ideally, install enough sample probes to resolve significant inflections in O_2 and/or CO_2 concentrations with depth.

4.2.2 Establishing Concentration Gradient Control Points

Figure 4-2 depicts potential soil gas concentration profiles for Scenarios A and B. Even in an ideal setting (i.e. homogeneous, isotropic, static equilibrium), the gas concentration gradients may not be linear. For O_2 , the concentration gradient tends to steepen near the ground surface and flatten near the bottom of the hydrocarbon oxidation zone where O_2 becomes significantly depleted. (In this context, a steep chemical gradient is a relatively

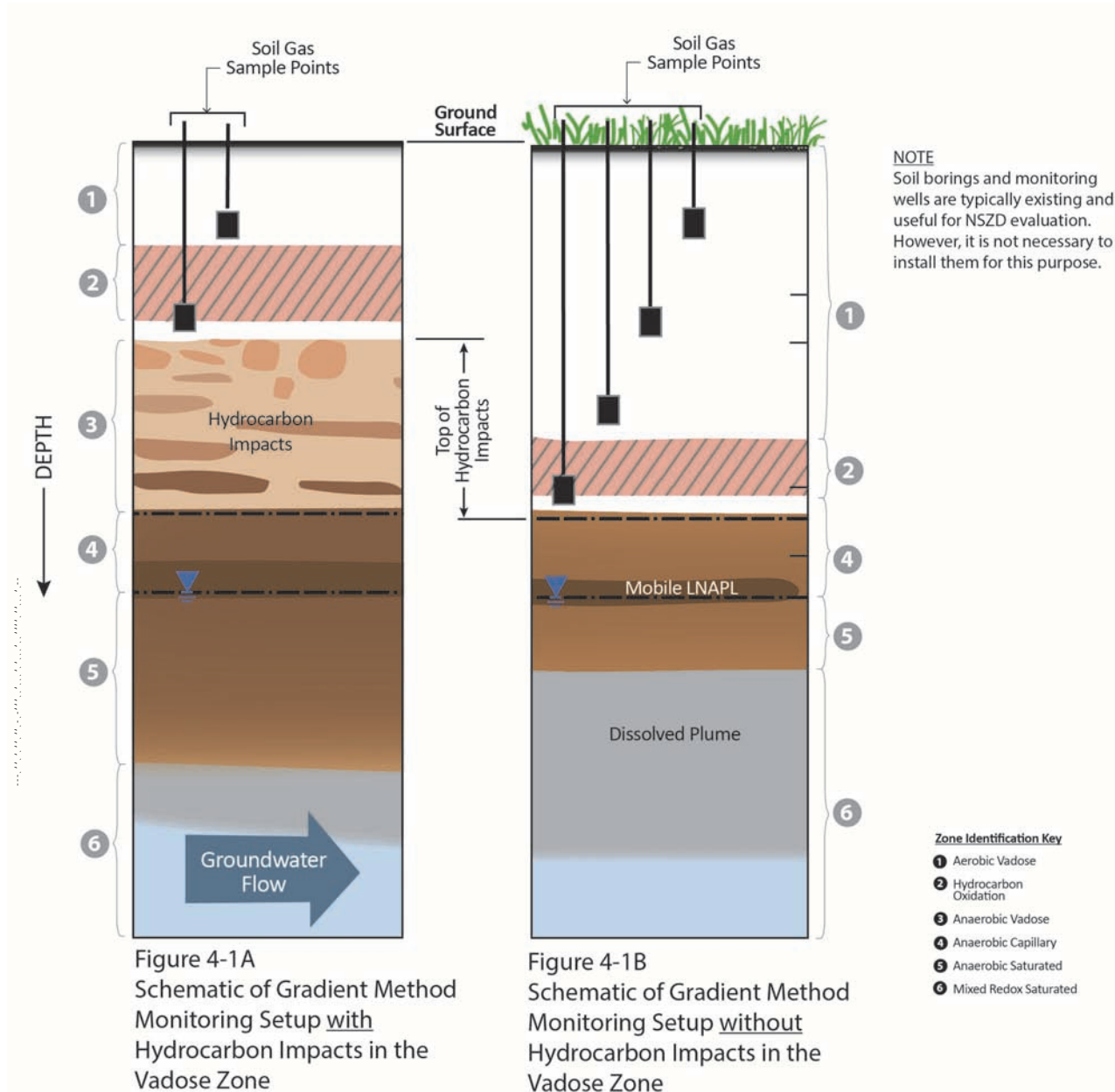


Figure 4-1—Schematic of Gradient Method Monitoring Setup with (a) and without (b) Hydrocarbon Impacts in the Vadose Zone

large change in concentration over a unit change in depth or elevation. Conversely, a flat chemical gradient is a relatively small change in concentration over a unit change in depth or elevation.) For CO_2 , the variation in concentration gradient with depth is somewhat similar although concentration profiles of CO_2 and O_2 are often a mirror image of each other. O_2 concentration is highest at the ground surface and lowest near the source zone, while CO_2 tends to be lowest at the ground surface and highest just above the source zone.

Concentration variations may occur near the ground surface due to the influences of temperature, root zone biological activity, and soil moisture. These effects would be most pronounced in a soil with surface vegetation as depicted in Scenario B. In these ideal settings (i.e. Scenarios A and B), there is a depth where the gradients and fluxes become less variable. This depth is generally below the vegetative root zone and above the hydrocarbon oxidation zone. This

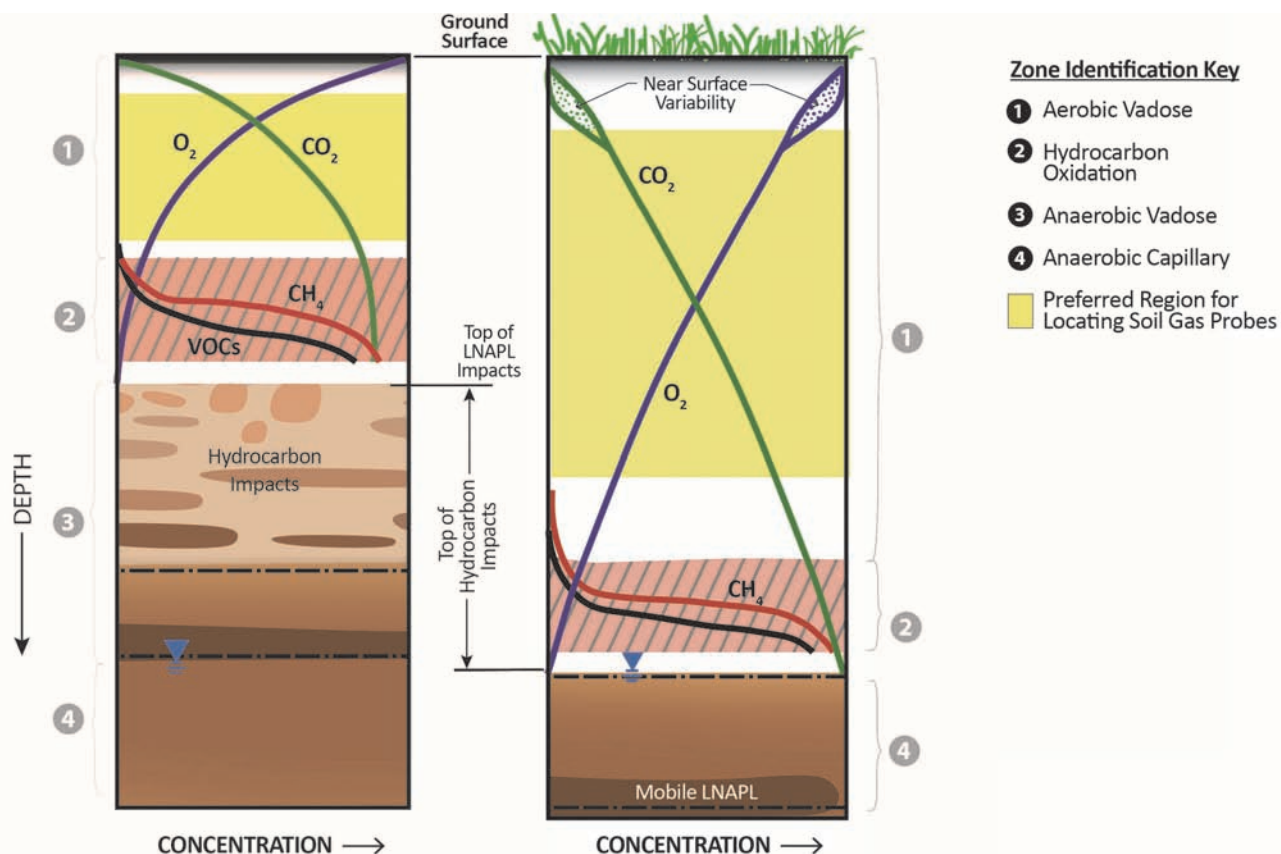


Figure 4-2—Conceptualization of Soil Gas Concentration Profiles with (a) and without (b) Hydrocarbon Impacts in the Vadose Zone

is the preferred region for locating soil gas probes for concentration gradient estimation, as indicated in yellow shading on Figure 4-2. In this sense, the gradient method may be less susceptible to near-surface influences than the surface-based NSZD methods.

Moving deeper into the vadose zone, a common challenge is that the position of the hydrocarbon oxidation zone is unknown prior to installation of soil gas sampling probes. Good judgment is needed to anticipate (and then verify) its depth. Recent releases (early stage, unweathered), less permeable soils in the upper portion of the vadose zone, high rates of subsurface CH_4 generation, and extensive lower permeability ground surface cover will tend to shift the hydrocarbon oxidation zone to shallower depths. Conversely, older releases (middle- to late-stage, weathered), more permeable soils, and open ground surface cover will tend to shift the interface closer to the top of the petroleum hydrocarbon-impacted soils.

The hydrocarbon oxidation zone (Zone 2) can be identified as the depth interval where O_2 concentrations diminish to effectively zero (e.g. less than 1 % to 2 %) and CO_2 concentrations approach a maximum. Elevated CH_4 with an absence of O_2 is an indicator that a location is below the hydrocarbon oxidation zone. Review of existing soil boring logs containing soil headspace VOC data can be used to estimate the depth to the top of the hydrocarbon impacted soil (Zones 3 and 4) and the hydrocarbon oxidation zone inferred to lie above it. In some cases, soil descriptions can be used to identify the oxidation zone where lithology transitions to lower permeability and higher moisture content soils or where soil color goes from oxidized (reddish) to reduced (dark brown or black in color). Temperature vs depth profiles may also indicate the approximate position of Zone 2, which tends to coincide with elevated temperature from biogenic heat production (see 7.1.2). If a hydrocarbon oxidation zone is not apparent in the data, then additional data collection may be necessary to revise the LCSM.

The concentration gradient can be thought of as the slope of a line drawn between two points (depths) in the subsurface, an upper boundary control point and a lower boundary control point.

The concentrations of O_2 and CO_2 at the ground surface at most exterior locations can be reasonably approximated by those of ambient air. Soil gas concentrations at the ground surface (zero depth) can be assumed to be in equilibrium with the concentrations in ambient air: O_2 at 20.9 %, and CO_2 at 0.03 %. These are the upper boundary control points for the gradient method.

In combination with using the ground surface as the upper boundary control point, a single probe at the “right” subsurface depth (i.e. at the lower boundary control point) can define a gradient with reasonable accuracy. This is illustrated in Figure 4-3. The three green dots in Figure 4-3A show three choices for the location of the CO_2 gradient lower control boundary point. The “right” control point would be located at the middle green dot labeled as “Gradient accurately estimated”. Similarly, the blue dots in Figure 4-3B show three choices for the O_2 gradient lower control boundary point, with a lesser difference in gradients, but the middle being preferred.

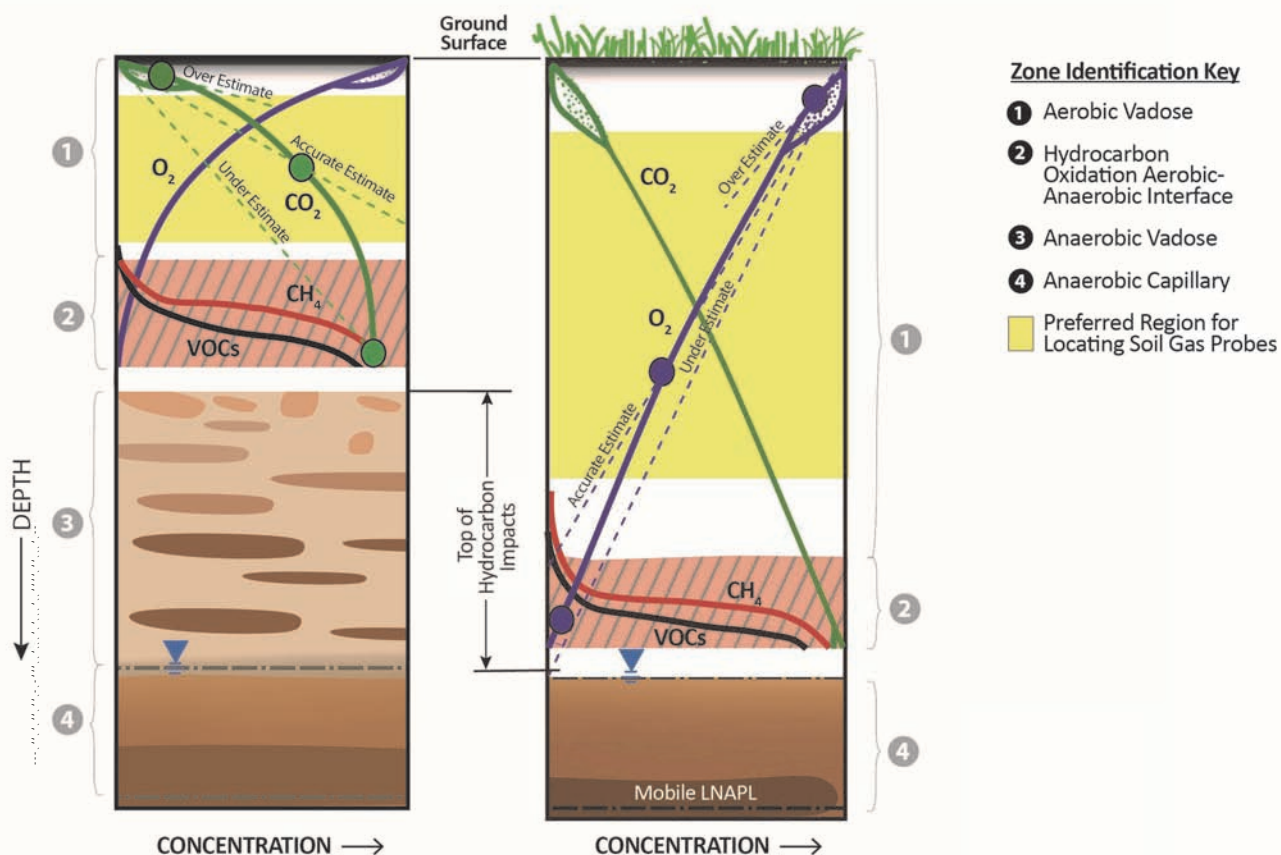


Figure 4-3—Choice of Measurement Points and Influence on Estimated Gradient CO_2 Gradient in Soil with (a) and without (b) Hydrocarbon Impacts in the Vadose Zone

In practice, the best position for the lower boundary control point measurement is usually not known a priori. As illustrated in Figure 4-3, if points are used that lie along a shallow and steep portion of the chemical gradient, the gas flux and NSZD rate may be overestimated. Conversely, if points along the flatter, deeper part of the chemical gradient are used, the flux will be underestimated. The practical solution is to aim for an intermediate gradient, which can be obtained by using the ground surface as the upper control point, and one or more probes within the preferred region as the lower control points.

In this ideal setting (which assumes a constant D_{eff_v}), a lower control point located closer to (or below) the hydrocarbon oxidation zone will result in an underestimated chemical gradient, and consequently an underestimated NSZD rate (Figure 4-3). Because this is a conservative result, one potential strategy, in the absence of existing information to bound the hydrocarbon oxidation zone, would be to install the lower boundary control point close to the top of the petroleum hydrocarbon-impacted soil. (As described in 3.1.4, a monitoring well with a screen that spans the water table may be used to collect a soil gas sample for this purpose.) If hindsight shows this point to be positioned below the hydrocarbon oxidation zone, then the penalty is an underestimated NSZD rate.

4.2.3 Detection Limit Considerations

The gradient method is relatively insensitive to detection limits. The method only requires a sufficient concentration difference to reliably estimate the vertical concentration gradient. In practice, this does not usually pose a limitation because the concentrations of O_2 and CO_2 tend to change significantly and discernably from the typical 0.1 % by volume concentration detection limit of a field gas analyzer.

4.2.4 Measurement Timeframe

A single NSZD monitoring event using the gradient method is typically short in duration due to the quick measurement timeframe using field instrumentation and the short-term representativeness of the data when the temporal variability of D_{eff_v} is taken into consideration. Typically, the soil vapor concentration profiles at a single sample probe cluster location can be measured in approximately 1 hour. A network of up to 10 locations can typically be measured in a 1 day field effort.

4.2.5 Analytes

The analytes typically measured by the gradient method include O_2 , CO_2 , and CH_4 using a calibrated handheld multi-gas meter (e.g. Landtec GEM™5000). VOCs are also typically measured and can be performed in the field using an flame ionization detector (FID) (e.g. Foxboro TVA1000). An FID can measure parts per million concentrations of total VOCs and CH_4 with the addition of a carbon filter on the FID probe tip. Use of a nitrogen (N_2) analyzer can serve as a “check-sum” on the other gas results, because the sum of O_2 , CO_2 , CH_4 , N_2 , and total volatile hydrocarbons (VOCs) should approach 100 % (with Ar making up the balance and often incorrectly measured as O_2 on a laboratory gas chromatograph). If CH_4 is elevated at an unexpected location, consider collecting a gas sample for laboratory total petroleum hydrocarbon (TPH) analysis using modified EPA Method TO-15, for example, to determine the composition of the non- CH_4 gases. The presence of elevated non- CH_4 hydrocarbons may indicate a nearby petroleum source.

4.2.6 Sources of Uncertainty and Variability and Mitigation Plan

Some sources of uncertainty and variability, how those factors affect the concentration gradient and D_{eff_v} measurements, and suggested mitigation methods are summarized in Table 4-1.

The assessment of variability in NSZD rates is a site-specific consideration and the measurement program design should address each factor so that results can be more readily interpreted.

4.3 Field Monitoring

Consideration of the above factors will allow the user to design a robust gas flux monitoring program using the gradient method. In addition to the common implementation considerations discussed in 3.2, this section describes field implementation procedures unique to the gradient method.

4.3.1 Estimating D_{eff_v}

D_{eff_v} is a critical parameter to the gradient method. The significant spatial and temporal variation of water content in the unsaturated zone means that D_{eff_v} and diffusive fluxes may be expected to exhibit orders-of-magnitude variation

Table 4-1—Sources of Uncertainty, Variability, and Mitigations Associated with the Gradient Method

Factor	Affect	Mitigation
Effective diffusion coefficient, D_{eff_v}	Varies with soil moisture after rain events and seasonally	Perform diffusivity tests during the same field event with gas concentration measurements.
Variable topography and geologic conditions across the LNAPL footprint	Variable depths to the hydrocarbon oxidation zone will significantly affect the calculated fluxes	Measure D_{eff_v} and soil gas concentration profiles at each multilevel soil gas sample probe within each unique area of the site.
Short measurement period	Only a snap shot in time of what can be a dynamic soil gas profile	Perform additional measurements at different times of the year to ascertain the variability.
Analytical calculation assumes only diffusive flux	Advective fluxes, those driven by pressure gradients, are neglected by the method	Verify that advection is negligible (i.e. pressure differentials in soil column are negligible).

over limited spatial and temporal scales (Tillman and Smith 2005; Wealhall et al. 2010). Therefore, in a layered unsaturated zone, vapor diffusion from depth to the ground surface is typically limited by the wettest or least porous soil layer. At some sites this may occur in the shallow vegetated soil where it is directly impacted by precipitation events. At other sites with coarse overburden, the wettest or least permeable zone may occur within a finer-grained lithology deeper in the vadose zone. It is incumbent on the practitioner to select the appropriate D_{eff_v} , or range of D_{eff_v} , based on site-specific conditions. Some guidance on parameter estimation and measurement is provided below.

D_{eff_v} can be estimated from empirical correlations such as Millington and Quirk (1961; see Equation 3.1 in 3.1.4), but preference is given to in situ measurement because the majority of soils are not homogeneous and isotropic. A review of six empirical models used to estimate D_{eff_v} in shallow soil from soil water content, porosity, particle size distribution, and bulk and particle density was performed (Pingintha et al. 2010). The modeled D_{eff_v} results were then applied to estimate CO₂ efflux using Fick's law and compared to field measurements made using a DCC. The study results showed significant deviations in the estimated soil CO₂ efflux with all methods except one, the Moldrup et al. (1997) model. For example, the Millington and Quirk (1961) method gave a 58 % error as compared to the flux measured using a DCC. The Pingintha (2010) paper goes on to recommend a weighted harmonic averaging technique to generate a better empirical estimate of D_{eff_v} . It follows in practice then, that empirical estimates of D_{eff_v} are only recommended for qualitative or screening-level assessment of NSZD using the gradient method. For quantitative NSZD evaluations, site-specific measurements at each multilevel soil gas sample port are recommended to be completed at the same time that the soil gas concentration profiles are measured.

4.3.1.1 Site-specific D_{eff_v} Measurements

In their vapor intrusion guidance, the California Department of Toxic Substances Control (DTSC) recommends direct field measurement of D_{eff_v} and air permeability over determination of these fate and transport parameters by other means (CalEPA 2011). As it also pertains to evaluation of NSZD, to reduce uncertainty about scale effects and soil sample representativeness, practitioners should consider measuring D_{eff_v} in the field.

Site-specific D_{eff_v} can be determined by an in-situ tracer method described by Johnson et al. (1998). A known volume of air spiked with a known concentration of a tracer gas such as helium or SF₆ (typically several thousand parts per million by volume) is injected into the vadose zone at various depths using the same multilevel soil gas probes used to profile soil gas concentrations. After a period of time, typically less than one hour, the same volume of soil gas is extracted from each probe, and the recovered tracer concentration is determined. Appendix A contains an example implementation procedure for measuring D_{eff_v} in situ. By comparing the initial and final tracer concentrations, the sample volumes, and the test duration, the quantity of the effective diffusion coefficient for the tracer gas ($D_{eff_{tracer}}$) is determined.

The D_{eff}^v can be estimated using a nonreactive (inert), nonsorbing, tracer gas with a high Henry's Law constant and diffusion-dominated chemical transport in a porous, homogeneous, isotropic medium (Johnson et al. 1998). For a point source, the effective diffusion coefficient D_{eff}^{tracer} (m^2/s) for the tracer gas can be estimated using Equation 4.2:

$$D_{eff}^{tracer} = \left[\frac{\theta_v}{\beta} \right] \left[\frac{1}{4t_s} \right] \left[\frac{3V_s}{4\pi} \right]^{\frac{2}{3}} \quad (4.2)$$

Where θ_v is the air-filled porosity (m^3 -vapor/ m^3 -soil), t_s is the sampling time [s], and V_s is the volume of vapor extracted at the end of the test (m^3). The value of β is determined by graphical or iterative approximation as shown on Figure 4-4 where V_o is the volume of tracer gas originally injected (m^3).

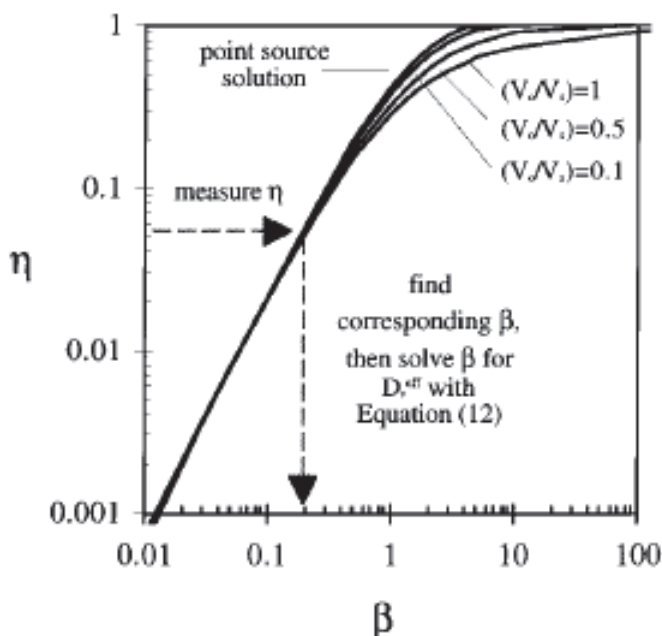


Figure 4-4—Determination of β Parameter in Equation 4.2 from Nonreactive Tracer Test Measurements of Mass and Vapor Recovery
(Excerpt from Johnson et al. 1998)

Knowing D_{eff}^{tracer} allows $D_{eff}^{O_2}$ to be calculated by correcting for the difference in molecular diffusion coefficients in air D_{air} using Equation 4.3:

$$D_{O_2}^{eff} = D_{eff}^{tracer} \left(\frac{D_{O_2}^{air}}{D_{air}^{tracer}} \right) \quad (4.3)$$

Where $D_{O_2}^{air}$ is the molecular diffusion coefficient for O_2 (m^2/s) and D_{air}^{tracer} is the molecular diffusion coefficient for the tracer gas (m^2/s). D_{eff}^v for the gas of interest (i.e. O_2 or CO_2) is calculated by multiplying D_{eff}^{tracer} by the ratio of molecular diffusion coefficients in air of the gas species (D_{air}^v) of interest ($O_2=0.205 \text{ cm}^2/s$, $CO_2=0.155 \text{ cm}^2/s$, $CH_4=0.220 \text{ cm}^2/s$) over the molecular diffusion coefficients in air of the tracer (D_{air}^{tracer} , helium= $0.703 \text{ cm}^2/s$, $SF_6=0.089 \text{ cm}^2/s$) (Lundegard and Johnson 2006; Werner and Hohener 2003).

For example, 1L of SF_6 tracer gas at 1,590 parts per million by volume (ppmv) was injected into a vapor sampling probe point. Fifteen minutes later, a 1L sample was taken from this same location and determined to contain 268 ppmv. The fraction recovered (η) was $268/1590 = 0.17$. Using a value of η of 0.17, and a V_o/V_s of 1, the β parameter was estimated using Figure 4-4 to be approximately 0.55. This value was combined with the estimated air-filled porosity θ_v (0.28), sampling time t_s (900 s), and volume sampled V_s (0.001 m^3) to calculate the effective vapor-phase porous medium diffusion coefficient for SF_6 (D_{eff}^{tracer}), which was calculated to be $0.013 \text{ cm}^2/s$. This result can be converted to $D_{eff}^{O_2}$ by multiplying by 2.3, the ratio of the molecular diffusion coefficient for O_2 to the molecular

diffusion coefficient for SF₆. The final calculated effective vapor-phase porous medium diffusion coefficient for O₂ for this sample point was 0.03 cm²/s.

If estimates of D_{eff_v} are obtained within multiple soil layers, then a thickness-weighted harmonic average to estimate overall effective D_{eff_v} across the soil depth range of interest can be calculated as shown on Equation 4.4 (Pinging et al. 2010):

$$D_v^{\text{eff}} = \frac{\sum_{k=1}^n \Delta z_k}{\sum_{k=1}^n \frac{\Delta z_k}{D_{sk}^{\text{eff}}}} \quad (4.4)$$

Where D_{sk}^{eff} represents the effective vapor diffusion coefficient for the discrete layer k with thickness Δz , and n is the number of measured layers within the soil profile.

After completion of the diffusivity tests, the results should be verified against literature values. If results differ significantly, then review the data and soil conditions (i.e. moisture) at the time of measurement and repeat measurements if necessary. Comparison of historical measurements will facilitate a better understanding of the parameter.

4.3.2 Collecting Samples from the Probes

Sample collection from the probes for soil gas monitoring is typically done using active soil vapor sampling methods and is often subject to site-specific guidelines or procedures. If no project- or site-specific soil vapor sample collection QA/QC requirements exist, then several resources may be consulted including ITRC's petroleum vapor intrusion guidance (ITRC 2014) and API (2005), *Collecting and Interpreting Soil Gas Samples from the Vadose Zone*. They include specific recommendations on the sampling of temporary and permanent soil vapor monitoring probes.

4.3.3 Cold Weather Equipment Considerations

Cold weather (i.e. daytime ambient temperatures below 32 °F/0 °C) concerns when performing soil gas concentration measurements include proper instrument operation and maintaining vapor flow through vapor probes and tubing that may contain frost or ice. Prior to collecting samples, ensure the sample probe tubing is clear of obstructions and vapor flowing similar to how it would in warmer times. Necessary precautions should be taken to ensure that field gas analyzer and other equipment is maintained in functional condition, tubing kept free of moisture and ice, and batteries are kept charged.

4.3.4 Quality Assurance/Quality Control

Appropriate QA/QC measures are essential to assess the accuracy and precision of the data collected. Use proper, manufacturer-recommended calibration procedures for all field instruments. A minimum two-point calibration is typically prudent with a span gas calibrated to the range of expected concentrations. Field and laboratory samples should comply with project-specific duplicate sample collection as well as ambient field blanks, if samples are to be sent to a laboratory.

4.3.5 Daily Logs and Record Keeping

Record soil gas sampling procedures and results as would normally be required by site-specific field work protocols. Example field data collection forms are included in Appendix A for D_{eff_v} test and soil gas concentration measurements. Some of the more important fields to record include: verification of probe depth, probe leak detection parameters, purge flow and duration, and field measurement results of fixed and combustible gases. Of particular note, if field VOC and CH₄ measurements are planned, record FID measurements for each sample with and without a carbon filter placed on the instrument probe tip. Documentation of ambient weather conditions is also very important and should be recorded at each sampling event.

4.4 Data Evaluation

In addition to the common data evaluation considerations discussed in 3.3, field soil gas concentration profile data from the gradient method must be carefully handled to estimate the NSZD rates. This subsection discusses key gradient method-specific data evaluation steps.

4.4.1 Estimating the Concentration Gradient

Approaches to estimating the concentration gradient will vary with the number and depth of sample probes and is discussed in detail in 4.2.2. All the approaches are based on the same basic principle, however. The numerical difference in concentration between the upper and lower boundary control points of measurement, divided by the vertical distance between the control points, gives an estimate of the vertical concentration gradient (dC/dz) as shown by Equation 4.5:

$$\frac{dC}{dz} = \frac{C_2 - C_1}{z_2 - z_1} \quad (4.5)$$

C_1 and C_2 are the gas concentrations at depths z_1 and z_2 , respectively.

If using just two boundary control points, then subtract one concentration from the other, then divide it by the vertical distance between the two sampling probe midpoints or the depth to the lower sample probe midpoint from the ground surface (e.g. if the ground surface is used as the upper and a single “right” depth as the lower control point).

If more than two soil gas measurement depths are available, as may be the case with a multi-level probe cluster or nest, in most instances, it is not advisable to make multiple piecewise linear gradient estimations along adjacent probe pairs within the same probe cluster, then estimate an average gradient. Doing so tends to give greater weight to outliers, and deemphasizes the overall gradient trend, which is best selected using the logic described in 4.2.2. Doing this will ensure that the proper upper and lower boundary control points are used to define the NSZD-derived driving force for diffusion through the vadose zone. The exception would be if D_v^{eff} has been determined at comparable depths, and the variations in D_v^{eff} align with the variations in the concentration trends. Recall that the gradient method assumes that gas flux is in a steady-state, which means that the magnitude and direction is assumed similar through all soil layers. Thus zones of lower D_v^{eff} are assumed to have steeper chemical gradients, and vice-versa.

4.4.2 Calculating the Gas Flux

To calculate the gas flux, multiply its D_v^{eff} by its concentration gradient as shown by Equation 4.6:

$$J = D_v^{eff} \frac{dC}{dz} \quad (4.6)$$

This gives the gas flux in units of mass per area per time (e.g. $\mu\text{mol}/\text{m}^2/\text{s}$). This calculation can be performed for any of the measured gases O_2 , CO_2 , and/or CH_4 .

4.4.3 Converting Gas Flux to Mass Loss

Section 3.3.2 demonstrates how to estimate an NSZD rate from the gas flux. The NSZD rate can be calculated using the CO_2 efflux and O_2 influx results alike. To adapt the calculation for O_2 , multiply the O_2 gas influx by the stoichiometric ratio with the hydrocarbon obtain the NSZD rate.

4.4.4 Typical Data Evaluation Challenges

After review and analysis of the gradient method results, the user may find that the data did not produce results as expected or may be inconsistent with results from initial NSZD screening (see 3.1.4). Some items to consider when trying to understand anomalous data include:

- changes (geospatial and/or temporal) in soil moisture can significantly affect the measured soil gas profiles;
- an inconsistent vadose zone, e.g. containing a low diffusivity zone or peat layers, will effect soil gas profiles;
- the gradient method measurement is considered a “snap shot” in time;
- incorrect selection of the lower boundary control point.

Any of the above factors can influence the calculation of O₂ influx/CO₂ efflux and thus the estimated NSZD rate at a site. If data interpretation challenges arise, then the reader is advised to review this section of the document as many of the impacts of these issues are discussed herein. Additionally, the reader is advised to review Section 3 for discussion of key LCSM elements and review inaccuracies in site-specific assumptions that went in NSZD monitoring program design. In most situations, the data can be resolved and useful results obtained after careful data review and optimization of parameters and calculations.

5 Passive Flux Trap Method

The passive flux trap method is largely derived from adaptations to a static chamber design. It was historically fitted with a chemical trap to measure soil-surface CO₂ flux (Humfeld 1930; Edwards 1982; Rochette and Hutchinson 2005). The passive flux trap method was recently adapted for NSZD monitoring (McCoy et al. 2014). It was developed by Colorado State University and Chevron U.S.A. and patented (U.S. Patent No. 8,714,034). It was commercialized and further refined by E-Flux, LLC (Fort Collins, Colorado) and employs the use of a sorbent to collect gases leaving the subsurface.

5.1 Description

The trap setup is composed of three main parts: the trap body, receiver pipe, and rain cover. The traps are installed in the shallow ground surface and left in-place for a multi-day timeframe. Over this time, CO₂ migrating upward from the subsurface to the atmosphere is collected by a caustic sorbent material. To prevent measuring atmospheric CO₂ that would bias soil gas efflux measurements, a two-layer system is employed in the trap. The trap is constructed with a bottom sorbent material layer to collect CO₂ derived from the subsurface and an upper sorbent material layer to collect atmospheric CO₂ when gas flow reverses due to barometric changes. The trap is deployed for a period of time that does not allow for either the top or bottom layers to become saturated with CO₂, thereby preventing cross contamination of CO₂ between atmosphere and subsurface. The bottom of the trap is open to the subsurface and the top of the trap is open to the atmosphere and the entire system designed to minimize impacts on the atmosphere/soil gas interaction. The CO₂ trap is placed on a receiver pipe that is installed into the shallow ground surface. This receiver pipe provides an anchor point for the CO₂ trap body. The trap body is attached to the top of the receiver pipe with a rubber sleeve that is impervious to lateral gas flow. A rain cover prevents water from entering the trap and interfering with sorption. A schematic diagram of a passive CO₂ flux trap is shown in Figure 5-1.

5.2 Program Design Considerations

In addition to the common program design considerations discussed in 3.1, a number of additional factors are considered when designing a CO₂ efflux survey using the passive flux trap method.

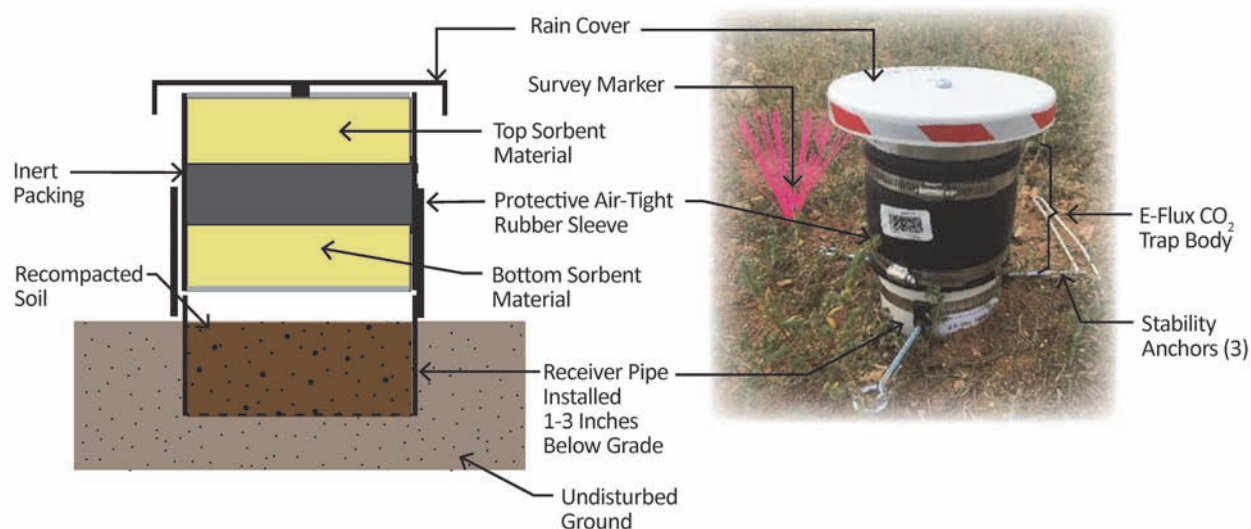


Figure 5-1—Schematic (Left) and Photo (Right) of a Passive CO₂ Flux Trap

5.2.1 Location Selection and Data Density

Traps are a tool to determine the petroleum hydrocarbon-derived CO₂ efflux at particular locations of interest across the LNAPL footprint. The spatial coverage achievable using the passive flux trap method can be limited because it uses a commercial device that requires offsite laboratory analysis. A network of traps can be costly to install and analyze, and depends significantly on the number of locations and chosen analyses (e.g. CO₂ and ¹⁴C). An acceptable number of traps is assessed on a site-specific basis by weighing the data objectives of the NSZD monitoring program against other site and project constraints. For example, when carefully co-located in consistent soils with the gradient or DCC methods, passive flux traps can be installed at select few locations and used for QA/QC purposes to provide support for efflux measurement validation or background correction.

LNAPL distribution, geologic, and groundwater hydraulic information from monitoring wells and soil borings can help inform the selection of CO₂ efflux survey locations. In general, it is suggested that traps be co-located with existing groundwater monitoring wells and/or historical soil borings in order to correlate results to known subsurface information.

At a minimum, it is generally advised to perform trap measurements within each unique source area at the site. Zones of common LNAPL, geologic, and hydraulic characteristics can be delineated and assigned to individual trap locations accordingly. Additional trap installations can be located in areas that may exhibit different LNAPL weathering rates such as upgradient, mid-plume, and downgradient locations.

Placement of efflux survey locations should also take into account ground surface conditions, particularly as they relate to indications of recent surface spills or staining. Minor surface or shallow subsurface staining associated with more recent spills can cause CO₂ efflux values to be anomalously high and would overestimate flux associated with the main LNAPL body.

As with other methods to measure gaseous efflux at ground surface (e.g. DCC), passive flux trap locations also need to be located in soils that can permit gas transport. If they are installed within impervious or compacted or low permeability zones and penetrate a layer confining to the underlying soil vapor, then a chimney will be created and results will be non-representative of natural gas efflux. As such, they should not be installed in concrete or asphalt pavement, or very hard compacted soils. Surface vegetation should also be removed from beneath the trap location prior to installing the receiver pipe.

Installation of passive flux traps in background locations is not necessary if ^{14}C correction is used. As described in detail below (see 5.4.2), isotopic correction can be performed on the traps atop the LNAPL footprint and eliminate the need for separate traps in background, unimpacted areas.

5.2.2 Detection Limit Considerations

The detection limit of the passive flux trap method is governed by the detection limit of the analytical method (i.e. carbonate analysis) used to measure the amount of CO_2 sorbed onto the caustic sorbent. The detection limit of a passive CO_2 trap can be estimated using a 5-times multiplier on the standard deviation as a reasonable range above which a measurement is valid, and a typical blank trap CO_2 content of 1 % by weight, and a typical coefficient of variation (cv) of 3 % on trap CO_2 analyses. The analytical detection limit of the CO_2 trap is approximately 0.15 % CO_2 by weight of the sorbent in the trap (i.e. 3 % cv $\times$ 1 % CO_2 by weight $\times$ 5). Using a typical deployment duration of 15 days and a trap cross-sectional area of a 4 in. diameter Schedule (Sch) 40 PVC receiver pipe and a sorbent mass of 40 grams, this equates to approximately 0.1 $\mu\text{mol}/\text{m}^2/\text{s}$. If the duration of the trap deployment decreases to 4 days, then the detection limit of the CO_2 trap method increases to 0.5 $\mu\text{mol}/\text{m}^2/\text{s}$. Laboratory results less than the estimated limit of detection are considered non-detect. Note that the detection limit will change with alternative capture areas and/or deployment times.

5.2.3 Deployment Timeframe

The deployment timeframe for passive CO_2 flux traps is determined by estimating the amount of CO_2 to be collected on the sorbent. The deployment timeframe is dependent on the expected CO_2 efflux and the quantity of sorbent material added to the traps. The caustic sorbent used in the traps has a 2 % detection and a 30 % saturation limit. The deployment period must be timed to ensure that the traps collect a mass of CO_2 within this operating range. A typical NSZD field event using the passive flux trap method entails deploying the CO_2 traps for approximately 2 weeks. When the actual mass of sorbed CO_2 exceeds the sorbent saturation limit of 30 %, as may occur for unusually large effluxes or extended deployment times, the analytical result must be qualified as low biased. When estimating the potential CO_2 efflux, account for both background and NSZD-derived CO_2 . In colder months, when natural soil respiration is low, for example, longer deployment times can be used.

5.2.4 Analytes

The only analytes currently measured using the passive flux trap method are CO_2 and ^{14}C . CO_2 is analyzed using open atmosphere acidification by ASTM 4373-02 (Rapid Determination for Carbonate Content in Soils). ^{14}C is run on the CO_2 that is captured from the acidification step and analyzed by ASTM D6686-12.

5.2.5 Sources of Uncertainty and Variability and Mitigation Plan

Some sources of uncertainty and variability, how those factors affect the measured CO_2 efflux measurement, and suggested mitigation methods for passive flux traps are summarized in Table 5-1.

The assessment of variability in NSZD rates is a site-specific consideration and the measurement program design should address each factor so that results can be more readily interpreted.

5.3 Trap Deployment and Retrieval

Consideration of the above factors will allow the user to design a robust CO_2 efflux monitoring program using the passive flux trap method. In addition to the common implementation considerations discussed in 3.2, this section describes some of the field implementation procedures unique to the passive flux trap method.

5.3.1 Installation Procedures

Once suitable locations are determined, hand-pick and remove shallow vegetation and large pieces of gravel or cobbles from the area prior to installation. Shallowly embed the Sch40 polyvinyl chloride (PVC) receiver pipe into the

Table 5-1—Sources of Uncertainty, Variability, and Mitigations for the Passive Flux Trap Method

Factor	Affect	Mitigation
Impervious ground cover or highly compacted, confining soil layers	Soil gas can migrate laterally in the vadose zone and is effected by various manmade and geologic materials.	Avoid impervious areas or areas with highly compacted, low permeability surface soil.
Wind effects	Wind can cause the passive flux trap method to over-estimate the actual efflux.	Although trap design is routinely reviewed and adjusted to provide more accurate results, at sites with excessive winds, monitor wind speeds and consider correcting results for elevated wind speeds (Tracy 2015 and E-Flux 2015).
Precipitation during deployment	The rain cover on the trap assembly may prevent wetting of underlying soil, causing a rain shadow in which preferential flow can develop. Research is ongoing to determine effect of precipitation on trap measurements.	Minimize deployment duration and time of year with respect to rainfall events. Turn off irrigation systems during deployment, if possible. Avoid rainfall events and wait until a dry period, preferably a week or more after a heavy rainfall. Limit trap installation depth.

ground surface approximately 2 to 3 in. Push the receiver pipe plumb into the ground by hand into soft ground or using a rubber mallet for hard ground. For more compacted or rocky soils, it may be necessary to dig a small hole to install the receiver pipe. Take care to minimize disturbance of the surrounding soil which could create preferential pathways of soil gas flow and cause potentially erroneous measurements. Secure the receiver pipe in the ground by using stakes and stabilizers, if necessary. Following receiver pipe installation, recompact the soil inside and outside the pipe to pre-existing conditions by using a manual standard compaction slide hammer or other standard procedure (see 3.2.3). Installing the receiver pipes to a consistent depth is important to provide comparable data across the survey network at the site. If traps are installed at different depths, and some penetrate through ground surface layers that are confining to underlying soil vapor (creating a preferential gas pathway, or “chimney”) and others do not, for example, then it may generate inconsistent and variable results. Remove the shipping caps from the passive flux traps and fasten the trap to the top of the receiver pipe. Finally, attach the vented protective rain cap to the top of the trap to protect the sorbent from precipitation. Figure 5-1 shows a completed CO₂ trap assembly as-installed in the field. Appendix A contains an example implementation procedure for installing the receiver pipes and traps.

Apply careful and consistent procedures to increase the likelihood that the same condition is achieved for each installation. Following standard procedures, such as recompaction, for receiver pipe installation increases the likelihood that each receiver pipe is installed in a very similar fashion and the trap measured flux is representative of actual flux coming out of the ground at that particular location. Following standard procedures also improves comparison with other CO₂ flux monitoring methods, such as the DCC method (see Section 6). Following installation of the traps, record soil conditions and photo document the final installation.

5.3.2 Cold Weather Equipment Considerations

There are minimal cold weather concerns with the equipment when performing CO₂ efflux measurements using the passive flux trap method. Added effort may be needed to ensure that a good seal is made with the rubber fitting between the receiver pipe and the trap assembly. If the materials are cold, they may be rigid and require additional effort to form a good seal.

5.3.3 Quality Assurance/Quality Control

Appropriate QA/QC control measures are essential to assess the accuracy and precision of the data collected. A minimum of one duplicate trap location per every 10 locations is recommended. The duplicate trap should be installed in the same manner as the original location and placed no more than approximately 2 ft from the original location, in similar ground cover. Basic statistics including the calculation of a relative percent difference (RPD) from the original and duplicate sample data are performed to assess data quality. An RPD greater than 30 % may prompt the user to

assess the soil receiver pipe installation procedures to ensure a good seal with the subsurface was attained. This is considered an RPD target only, heterogeneities present in the soil may hinder the ability to achieve it at many sites.

Additionally, a trip blank, provided by the laboratory, is shipped, processed, and analyzed along with all the samples for each field event to account for sorbed CO₂ not associated with flux from the subsurface (see 5.4.1).

5.3.4 Daily Logs and Record Keeping

A suggested field sampling sheet template is included in Appendix A. Some of the more important fields on the sampling sheet template include: soil receiver pipe installation details (including installation method, date, depth, soil type, and soil conditions during installation), measurement data which includes date/time, location, and ground cover details. Documentation of ambient weather conditions is also very important and recorded at each deployment.

5.3.5 Trap Retrieval and Lab Analysis

After the appropriate deployment time, the passive flux traps are taken off the receiver pipes and original caps placed securely back on the top and bottom. They are then logged into the chain of custody form and shipped to a laboratory for analysis. Appendix A contains an example implementation procedure for retrieval of the traps. CO₂ is analyzed for total carbon using a standard method, for example by ASTM 4373-02. ¹⁴C is analyzed by ASTM D6686-12. The receiver pipes can either be left in place (and protected) for future monitoring or removed and ground surface restored to original conditions.

5.4 Data Evaluation

In addition to the common data evaluation considerations discussed in 3.3, raw total CO₂ efflux data from the traps must be carefully handled to estimate the NSZD rates. This subsection discusses key trap-specific data evaluation steps.

5.4.1 Trip Blank Correction

The first step in CO₂ trap data evaluation is to subtract the trip blank CO₂ mass from the sample results. Before deployment, each trap contains a small amount of CO₂ accumulated during manufacturing and transport. A trip blank is used to quantify it and provide a data basis to eliminate it from the NSZD calculations. The trap results are trip blank (TB) corrected by using Equation 5.1:

$$\text{Avg. sample \% CO}_2 - \text{Avg. TB \% CO}_2 = \text{Corrected sample \% CO}_2 \quad (5.1)$$

The average values used in Equation 5.1 are calculated from laboratory replicate analyses.

5.4.2 Background Correction Using ¹⁴C

Unstable carbon isotope composition is an established quantitative basis (ASTM International Method D6866-16) that differentiates the fossil-based carbon input (e.g. from NSZD of LNAPL) from modern sources. Modern carbon is the subject of NSZD background correction and associated with plants/vegetation and other natural organic matter in the ecosystem. It is distinctly different from carbon derived from petroleum biodegradation as it is significantly younger than carbon derived from biodegradation of fossil-based petroleum hydrocarbon that originates from deep geologic reservoirs millions of years in age. Background correction using the radiocarbon technique relies on the analysis of ¹⁴C, an unstable carbon isotope with a half-life of approximately 5,600 years, that is generated by cosmic rays in the atmosphere. ¹⁴C is present in all living things including contemporary biomass, but it is absent from petroleum. Thus, modern organic carbon is ¹⁴C-rich, while fossil-based carbon is ¹⁴C-depleted. Furthermore, modern carbon samples and atmospheric samples have the same characteristic amount of ¹⁴C. The ability of accelerator mass spectrometry (AMS) to detect ¹⁴C enables quantification of the amount of modern carbon in a sample (Stuiver and Polach 1977).

As it pertains to background correction for an NSZD evaluation, AMS analysis of ^{14}C can be performed on CO_2 gas extracted from vapor samples. The CO_2 gas extracted from a vapor sample collected over an LNAPL footprint undergoing NSZD typically contains a mixture of carbon derived from modern and fossil origins. The results of ^{14}C analysis can be used to quantify the fraction of the carbon in the CO_2 that is derived from background (modern) and NSZD (petroleum) sources.

CO_2 samples are sent to an AMS lab for analysis. The laboratory reports the modern carbon fraction in the sample ($F_{m_{\text{sample}}}$). Assuming the carbon is comprised only of modern and fossil-based isotopes, a two source mass balance can be used to calculate the fossil fraction ($F_{f_{\text{sample}}}$). $F_{m_{\text{sample}}}$ can be estimated using Equation 5.2:

$$F_{m_{\text{sample}}} = (F_{f_{\text{sample}}} \times F_{m_{\text{fossil}}}) + [(1 - F_{f_{\text{sample}}}) \times F_{m_{\text{atm}}}] \quad (5.2)$$

where $F_{m_{\text{atm}}}$ is the fraction of modern carbon in the contemporary living material and equal to 1.05 (Hua et al. 2013). $F_{m_{\text{fossil}}}$ is the fraction of modern in the fossil-based carbon which is equal to zero as discussed above. Substituting these values into Equation 5.2, gives a solution for $F_{f_{\text{sample}}}$ as shown on Equation 5.3:

$$F_{f_{\text{sample}}} = 1 - \frac{F_{m_{\text{sample}}}}{1.05} \quad (5.3)$$

By convention, the ^{14}C analysis reports based on a 1950 National Bureau of Standards oxalic acid standard, synthesized when the ^{14}C atmospheric levels were lower than current due to nuclear testing. Due to reporting conventions, $F_{m_{\text{sample}}}$ is reported as if the analysis was done in 1950. Thus, $F_{m_{\text{atm}}}$ is counter-intuitively larger than 1.

5.4.3 Efflux Calculation

The CO_2 efflux is calculated by dividing the trip blank-corrected, fossil-based CO_2 mass sorbed (on bottom sorbent material layer) by the cross-sectional area of the receiver pipe ($8.11 \times 10^{-3} \text{ m}^2$ for 4 in. diameter Sch40 PVC) and the total in situ deployment time. Converting CO_2 mass to CO_2 efflux is calculated using Equation 5.4:

$$J_{\text{NSZD}} = \frac{g \text{ CO}_2 \left(\frac{1 \text{ mol CO}_2}{44 \text{ g CO}_2} \right) \left(\frac{1000000 \text{ } \mu\text{mol CO}_2}{\text{mol CO}_2} \right)}{\text{days deployed} \times 24 \frac{\text{hr}}{\text{d}} \times 3600 \frac{\text{s}}{\text{hr}} \times 8.11 \times 10^{-3} \text{ m}^2} = \frac{\mu\text{mol CO}_2}{\text{m}^2 \times \text{s}} \quad (5.4)$$

5.4.4 Typical Data Evaluation Challenges

After review and analysis of CO_2 trap data, the user may find that the data did not produce results as expected or may be inconsistent with results from other methods. Some items to consider when trying to understand anomalous data include the following.

- Soil moisture changes are more widely varying in shallow soil and may impact ground surface methods more than method implemented deeper in the subsurface such as the gradient method.
- The passive flux trap method represents a time-integrated efflux value whereas other methods are considered “snapshots” which may be higher or lower than the efflux values from the trap data depending upon weather conditions during the deployment.
- The use of ^{14}C is arguably the best, most quantitative means for background correction and it should be considered of utmost reliability.

Any of the above factors can influence the calculation of CO_2 efflux and thus the estimated NSZD rate at a site. If data interpretation challenges arise, then the reader is advised to review this section of the document as many of the impacts of these issues are discussed herein. Additionally, the reader is advised to review Section 3 for discussion of key LCSM elements and review inaccuracies in site-specific assumptions that went in NSZD monitoring program design. In most situations, the data can be resolved and useful results obtained after careful data review and optimization of parameters and calculations.

6 Dynamic Closed Chamber Method

A dynamic closed chamber (DCC) system is an active, specially adapted, direct measurement approach to estimate soil gas efflux at the ground surface. A DCC uses a small circulation of air between a chamber and a gas analyzer to monitor the increase in CO₂ concentration as a function of time. This change can then be used to calculate a gas flux. To minimize errors associated with pressure differential inside and outside the chamber, it is fitted with an engineered vent (Davidson et al. 2002). Chamber methods (including open/closed and static/dynamic methodologies) have been used to estimate shallow soil respiration for more than eight decades and remain the most commonly used approach in agriculture (Rochette and Hutchinson 2005). Of the multiple chamber designs that have evolved over that time, the DCC has been demonstrated to be a consistent efflux measurement method and used as reference for comparison to others (Norman et al. 1997). It was recently adapted for NSZD monitoring (Sihota et al. 2011).

6.1 Description

A DCC system typically consists of a survey chamber connected to a portable pump and CO₂ analyzer. For example, the LI-8100A (LI-COR Biosciences, Inc., Lincoln, Nebraska), uses an 8 in. (20 cm) survey chamber connected to a portable infrared CO₂ gas analyzer (IRGA). This survey chamber and analyzer unit is an automated system that can either collect rapid survey data (minutes) or perform long-term measurements and continuous monitoring (weeks to months). The LI-8100A uses a pneumatic, bellows-actuated and vented domed chamber, vapor pump, temperature/moisture analyzer, an IRGA, and control unit. The instruments can be controlled with a laptop computer or a smartphone application.

The basic equipment and setup of a DCC system is shown in Figure 6-1. The chamber is set on a soil collar which is shallowly embedded into the ground surface. The control unit automatically operates the chamber bellows, pump, and IRGA unit to perform efflux measurements. The pump and IRGA start and initiate a short period of pre-measurement purge. All cycles are controlled using user-definable timers. Following the purge cycle, the bellows is inflated to close the chamber atop the collar with an air-tight gasket. The pump circulates vapor through the chamber and back into the analyzer unit for CO₂, temperature, and water vapor measurement. The IRGA measures the change in CO₂ concentration in the vapor return line connected to the chamber.

A short, user-defined, deadband period (approximately 10 s to 20 s), the time interval to allow for steady mixing in the chamber after it closes, can be set to neglect the earliest time change in CO₂ concentration data. As further described in 6.4.2, it is the change in chamber CO₂ concentration over time after the deadband period that is used to estimate the CO₂ efflux. The water and temperature data are used to correct the measured CO₂ to a dry standard unit of measure. After the measurement period ends, the bellows deflates, the chamber is raised off the collar, and a post-measurement purge cycle is initiated. This process of bellows inflation, measurement, and bellows deflation continues until the preset number of measurements are collected at each location. The control unit then stops all function and allows the user to view the data and evaluate whether additional measurements are needed at the same location or whether measurement is complete. When measurements are complete, the user lifts the chamber and analyzer units, and moves to the next location to repeat the process.

Parameters used by the DCC system to calculate the soil CO₂ efflux include the following:

- chamber volume,
- collar area and height above ground surface (i.e. the offset),
- temperature,
- pressure,
- initial water vapor mole fraction,
- water-corrected CO₂ mole fraction.

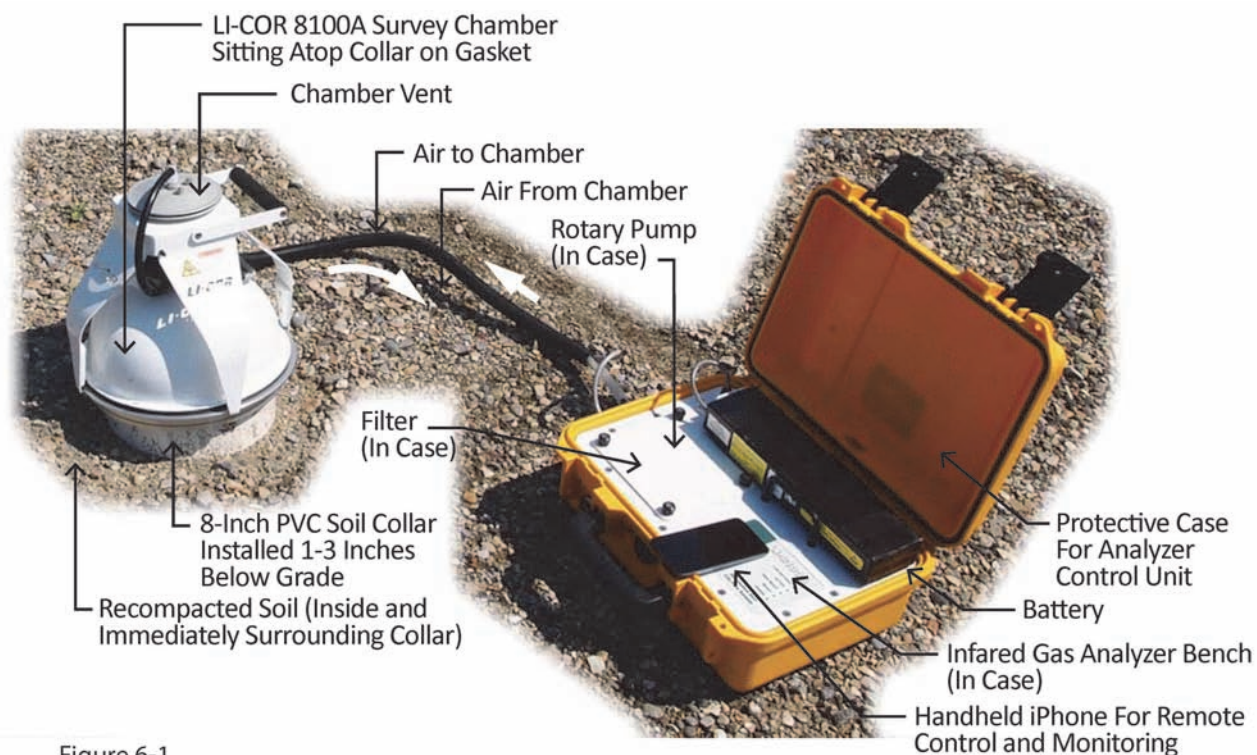


Figure 6-1

Figure 6-1—LI-COR 8100A DCC Apparatus and Setup

The collar height above ground (offset) is the only parameter that needs to be routinely measured by the field technician, all others are automatically calculated or measured by the LI-COR unit.

6.2 Program Design Considerations

In addition to the common program design consideration discussed in 3.1, a number of factors are considered when designing a CO₂ efflux survey using the DCC method.

6.2.1 Location Selection and Data Density

A common goal of placing CO₂ efflux survey locations is to obtain a geospatial distribution of measurements adequate to map the CO₂ efflux across the LNAPL footprint and also in a background area(s) for comparison. Data density is highly site specific, but in general, a number of survey collars are installed to both properly interpolate efflux across the petroleum hydrocarbon-impacted soils and effectively bound the outer limits of petroleum-hydrocarbon derived CO₂ efflux. Guidance is available from various authorities to help with selection of sampling locations (e.g. US EPA 2002).

LNAPL distribution data from sources such as historical release records, soil boring logs, and/or monitoring wells can help inform the selection of survey points. Co-locating survey points and background locations adjacent to monitoring wells both containing measureable LNAPL and also free of LNAPL is suggested as a first step in identifying survey points. Moreover, review of historical soil boring logs can be useful in understanding CO₂ flux data. It is critical that background locations be located in areas without petroleum hydrocarbons in soil, and wells in the background area should also preferably be free of dissolved hydrocarbon impacts. The user may find that interpolated CO₂ efflux values generally align with the LNAPL footprint as defined by observed presence in soil borings. A density of CO₂ efflux survey locations that is higher than monitoring wells may be used as indirect evidence of the presence or absence of LNAPL in areas without monitoring wells (Sihota et al. 2016).

6.2.2 Tailoring to Site Conditions

When designing an NSZD assessment using the DCC method, aerial photographs can be consulted and reviewed to identify ground cover types within the study area. Characterization of the ground cover and surface soil conditions is an important step in background correction to isolate CO₂ efflux from petroleum hydrocarbon sources. CO₂ efflux from the ground surface varies depending on the natural soil respiration and is a function of root zone and vegetation type (Rochette et al. 1999). Natural soil respiration rates vary and range from less than 1 to greater than 50 $\mu\text{mol}/\text{m}^2/\text{s}$ (Jensen et al. 1996).

Each CO₂ efflux survey location is classified by ground cover and vegetation type. Each ground cover type at locations atop the presumed LNAPL footprint requires at least one background survey location of the same ground cover and vegetation type outside of the LNAPL footprint for background correction (see e.g. Sihota et al. 2016). Two or more background survey locations outside the LNAPL footprint are helpful for assessing spatial variability of the background at a site. Background correction methodology is presented in the following 6.4.1.

Placement of NSZD survey locations should also take into account ground surface condition disturbances, particularly as they relate to indications of recent surface spills or staining. Minor surface or shallow subsurface staining associated with more recent spills can cause CO₂ efflux values to be anomalously high and would overestimate efflux associated with the main LNAPL body. Other disturbances of importance are historical trenches for utility installations, for example.

If the type of ground cover and ultimate placement of survey locations differ from originally planned based on aerial photography and previous knowledge of the site, these changes should be documented in the daily field log (see 6.3.4).

6.2.3 Detection Limit Considerations

The LI-COR 8100A IRGA is specified for an accuracy of 1.5 % of the measured CO₂ concentration, with a peak to noise ratio of approximately 2 ppmv. The limit of detection of the analyzer is 0.01 $\mu\text{mol}/\text{m}^2/\text{s}$, as found under a controlled experiment by LI-COR (LI-COR 2014).

Differences in atmospheric conditions influence the limit of detection of the LI-COR 8100A analyzer. To account for this, a CO₂ flux field blank is collected during each field event and a limit of detection is determined for that event. This is performed by attaching a sealed, closed collar that does not allow gas flow into the chamber (LI-COR 2014). A total of 60 readings are typically obtained for each field blank. Three times the standard deviation of the readings are then added to the average to obtain the limit of detection. Survey efflux values less than the field limit of detection are considered non-detect.

6.2.4 Deployment Timeframe

A single NSZD measurement using the DCC method is short in duration (approximately 1.5 minutes) due to the quick measurement timeframe of the IRGA and need to maintain the concentration gradient near the natural levels. Typically, a minimum of three sequential total CO₂ efflux measurements are made at a single location over a period of approximately 5 minutes. A network of 30 collars can typically be measured in a 1 day field effort.

6.2.5 Analytes

The only analyte typically measured by the DCC method is CO₂ and water vapor. However, concentrations of O₂, CH₄, VOCs, and other gases in the vapor within the chamber can also be measured using a supplemental trace gas analyzer connected in line with the survey chamber. The purpose of these measurements may vary from simple monitoring for presence/absence to estimation of their efflux alike done for CO₂. One example adaptation is to monitor the concentration of CH₄ in the chamber to evaluate the subsurface for the ample atmospheric exchange of O₂ and evaluate whether the majority of CH₄ that is created in the subsurface is oxidized to CO₂ prior to emission from the ground surface (see 3.1.3). This is an important measurement because it allows for validation of the CO₂

efflux method of estimating NSZD. If the gaseous byproducts of NSZD are only partially oxidized and some CH₄ is emitted, then the CO₂ efflux methods would be considered low-biased and underestimate the total amount of NSZD that is occurring. As discussed further in 7.2, the inclusion of CH₄ flux measurements at these sites would allow for a complete accounting of NSZD processes (Sihota et al. 2013).

6.2.6 Sources of Uncertainty and Variability and Mitigation Plan

Some sources of uncertainty and variability, how those factors affect the measured CO₂ efflux measurement, and suggested mitigation methods are summarized in Table 6-1.

Table 6-1—Sources of Uncertainty, Variability, and Mitigations Associated with the DCC Method

Factor	Affect	Mitigation
Irrigation or rainfall events	Changes natural soil respiration rate and inhibits gas transport.	Turn off irrigation system, if possible, or do measurements at the same time of day. Avoid rainfall events and wait until a dry period, preferably a week or more after a heavy rainfall.
Short measurement period and CO ₂ efflux subject to diurnal fluctuations	Only a snapshot in time of the CO ₂ efflux. Different CO ₂ efflux measured depending on time of day.	Assess diurnal variability through multiple measurements at various times of day at the same collar (e.g. morning, midday, and evening).
Impervious ground cover or highly compacted, confining soil layers	Soil gas can migrate laterally in the vadose zone and is effected by various manmade and geologic materials.	Avoid impervious areas or areas with highly compacted, low permeability surface soil.
Thick vegetation and elevated background CO ₂ efflux	Highly organic soils can create high CO ₂ efflux value which can mask NSZD-related efflux.	Use ¹⁴ C method of background correction (see 7.3) or perform efflux survey during colder, non-growing season.
Wind effects	Wind can cause the DCC method to underestimate the actual efflux.	At sites with excessive winds, monitor wind speeds and consider correcting results for elevated wind speeds (Tracy 2015).

The assessment of variability in NSZD rates is a site-specific consideration and the measurement program design should address each factor so that results can be more readily interpreted.

6.3 Survey Implementation

Consideration of the above factors will allow the user to design a robust CO₂ efflux monitoring program using the DCC method. In addition to the common implementation considerations discussed in 3.2, this section describes some of the field implementation procedures unique to the DCC method.

6.3.1 Installation Procedures

Once the survey locations are determined, an approximately 4 in. length of 8 in. diameter Sch40 PVC pipe is shallowly embedded into the ground approximately 1 to 3 in. to create a stable chamber mounting collar. The optimal collar depth will depend upon site conditions and the length of time the collars will be used at a given site (LI-COR 2015). At a minimum, the collar should be inserted into the soil to a depth that gives a solid foundation so the collar does not move when placing the chamber on the collar. An adequate insertion depth is also required to form a seal with the ground surface, eliminate direct gas exchange (i.e. chamber leakage) with the open atmosphere, and minimize lateral diffusion of CO₂ in the soil column below the chamber will be reduced. To reduce interference from CO₂ derived from “modern” or natural organic matter in soil, shallow vegetation is hand-picked and removed when

the collar is installed; surface soils could also be scraped back in an 8 in. diameter circle. Appendix A contains an example implementation procedure for installing the collar and performing the efflux measurements.

Set the collars in place a minimum of approximately 24 hours before the first measurement to allow for CO₂ vapor in the shallow soil to stabilize and minimize effects from soil disturbance occurring as a result of setting the collars in the soil (Jassel et al. 2012). Where site conditions allow, it is also recommended to leave the soil collars in place to allow for repeated measurements should preliminary data QA/QC identify issues with the data. If measurements at the same collar are to be repeated within a day, wait at least 20 minutes prior to performing the next measurement to allow re-equilibration of vapors in the shallow soil.

Take care to minimize disturbance of the surrounding soil that could create preferential pathways of soil gas flow and cause potentially erroneous measurements. Following collar installation, recompact the soil inside and outside the pipe to pre-existing conditions by using a manual standard compaction slide hammer or other standard procedure (see 3.2.3). Installing the collars to a consistent depth is important to provide comparable data across the survey network at the site. If collars are installed at different depths, and some penetrate through ground surface layers that are confining to underlying soil vapor (creating a preferential gas pathway, or “chimney”) and others do not, for example, then it may generate inconsistent and variable results.

Label and photograph the soil collars following installation. Before measurements begin, the offset (height of the collar top lip above ground surface) is measured in at least three locations along the inner circumference of the collar to enable an average volume estimate. This measurement is used to estimate the total volume of air inside the chamber and collar and is an important part of the overall efflux calculation. An average value of the offset measured from three sides of the collar are used to estimate the measurement volume as accurately as possible. Figure 6-1 shows a completed DCC CO₂ efflux measurement setup.

6.3.2 Cold Weather Equipment Considerations

Completing CO₂ efflux measurements using the DCC method in cold weather (i.e. daytime ambient temperatures below 32 °F/0 °C) presents unique challenges that the user should be aware of prior to initiation of the work. For example, a different method of collar installation may be required to obtain a good seal between the collar and frozen ground (see example collar installation procedure for frozen conditions in A.2). Frozen ground poses a unique condition that may preclude standard methodologies like compaction with a slide hammer. Like other modern, sensitive electronic equipment, cold weather can significantly reduce battery performance. Backup batteries should be kept onsite and warm (to the extent possible) in the event battery failure occurs. Cold weather can also affect the mechanical operation of the survey chamber itself. For example, close attention must be paid to the IRGA bench temperature remaining consistent at 50 °C or its specific setpoint. If necessary, the IRGA unit may be temporarily brought into a warm interior area to maintain proper instrument operation. Lastly, cold temperatures may affect the gasket seals between the chamber and the collar; make regular inspections and evaluate the results with this possible leak in mind.

6.3.3 Quality Assurance/Quality Control

Appropriate QA/QC control measures are essential to assess the accuracy and precision of the DCC data collected. Although periodic detailed and robust calibration is completed by most manufacturers of DCC systems under controlled factory settings, a span calibration of the instrument in the field is recommended prior to collecting field efflux data. Typically, this involves calibration to a 0 ppmv CO₂ standard (zero gas) and a span gas cylinder with a 500 ppmv CO₂ concentration.

A minimum of one duplicate efflux monitoring location per every 10 locations is recommended. The duplicate collar should be installed the same way as the original location and placed no more than approximately 2 ft from the original location, in similar ground cover and measurements should be collected at the same time of day. Basic statistics including the calculation of an RPD from the original and duplicate sample locations are performed to assess data quality. An RPD greater than 30 % may prompt the user to assess the soil collar installation procedures to ensure a

good seal with the subsurface was attained and evaluate the soils for any heterogeneities. This is considered an RPD target only, heterogeneities present in the soil may hinder the ability to achieve it at many sites.

At times, successive efflux measurements may have a lot of variability (e.g. not remain within 10 % of each other). In this situation, it is advisable to perform a second round of measurements at the same location. If measurements at the same collar are to be repeated within a day, wait at least 20 minutes prior to performing the next measurement to allow re-equilibration of vapors in the shallow soil.

Finally, a field blank is collected during each field event by attaching a closed collar that does not allow gas flow into the chamber. A total of 60 readings are obtained for each field blank. The results of the field blank are used to estimate the detection limit of the DCC system (see 6.2.3).

6.3.4 Daily Logs and Record Keeping

A suggested DCC monitoring field data sheet template is included in Appendix A. Some of the more important fields on the data sheet include: soil collar installation details (including installation method, date, depth, soil type, and weather conditions during installation), calibration results and setup details of the DCC instrument, and measurement data that include date/time, location, average offset measured from three points on the collar, ground cover details, efflux measurement and trace gas concentrations. Documentation of weather conditions is also very important and recorded prior to the start of each measurement at an individual location.

6.4 Data Evaluation

In addition to the common data evaluation considerations discussed in 3.3, raw total CO₂ efflux data from the DCC instrument must be carefully handled to estimate the NSZD rates. This subsection discusses key DCC-specific data evaluation steps. Appendix A contains an example implementation procedure for DCC data handling.

6.4.1 Background Correction

As discussed earlier in 3.1.6 and 6.2.1, a background correction is necessary to subtract natural soil respiration-derived CO₂ efflux from the measured total CO₂ efflux to isolate the NSZD-derived CO₂. If more than one background location is used for a particular ground cover, the arithmetic average of the CO₂ efflux value is calculated and subtracted from each survey location that is performed over or immediately adjacent to the LNAPL footprint in that same ground cover. This process is repeated for each ground cover type for which background survey locations were installed. The background efflux value is only valid for the particular field event in which successive CO₂ efflux measurements were taken. Future monitoring events would require the calculation of a background efflux value unique to that event.

6.4.2 Efflux Calculations

Using the DCC data collected, the CO₂ mole fraction corrected for water vapor dilution (i.e. the dry CO₂ concentration) is plotted against time (see Figure 6-2). The deadband (time before the vertical green line) and observation time (time between the vertical green and brown lines) can be adjusted where required to optimize the curve fit (R^2). Therefore, it is not critical if both the deadband and observation time are chosen incorrectly in the field, as long as the observation lengths are long enough to achieve a good curve fit.

Using the LI-COR, Inc.-supplied software (SoilFluxPro version 4.0 in 2016), the rate of CO₂ increase in the chamber is fit using either a linear or exponential regression. Jassal et al. (2012) found that a simple linear regression best represented imposed CO₂ efflux. In general practice however, the difference between linear and exponential curve fits is generally small. If a large disparity in curve fits and low R^2 values are observed, then a problem with the data set is likely and it should be more closely scrutinized before use.

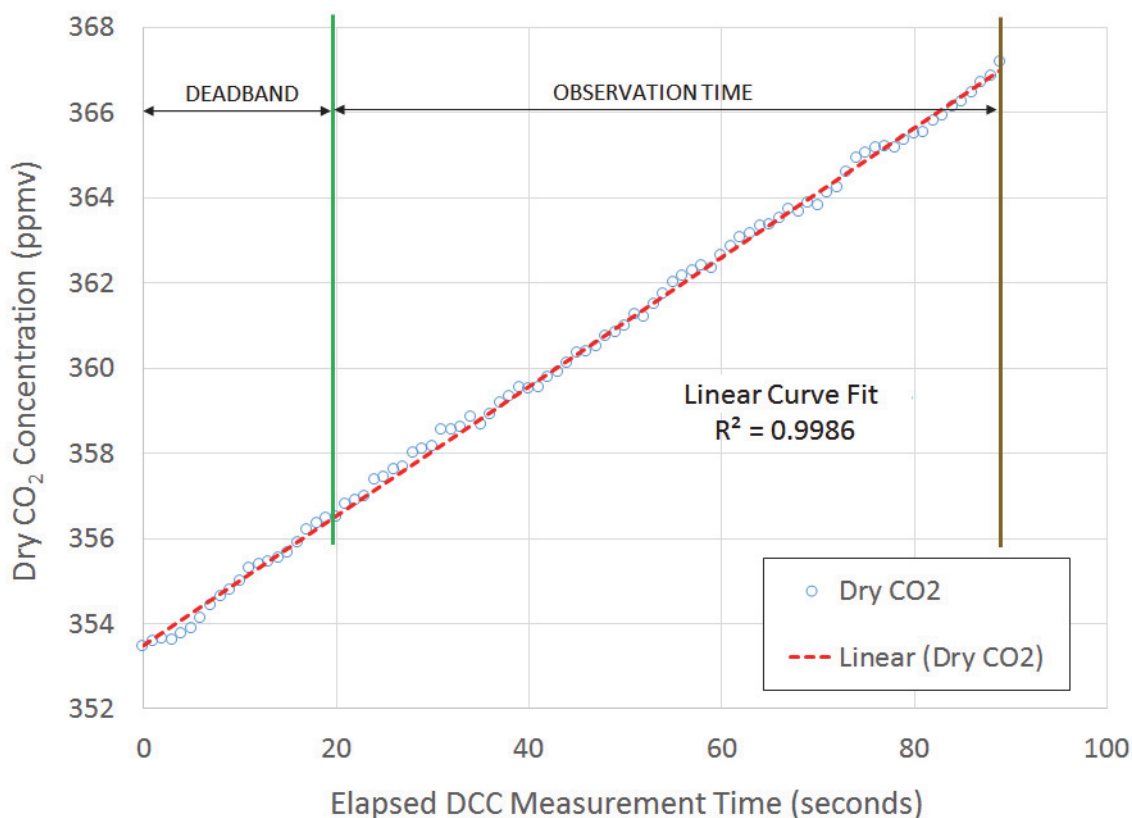


Figure 6-2—Example Output from a CO₂ Efflux Measurement Using a DCC

Once R^2 has been optimized, the equation of the exponential gradient is used to estimate the efflux as shown in Equation 6.1 as follows:

$$J_{Total} = \frac{10 \times V \times P_0}{R \times S \times (T_0 + 273.15)} \left(\frac{dC}{dt} \right) \quad (6.1)$$

where J_{Total} is the soil CO₂ efflux ($\mu\text{mol}/\text{m}^2/\text{s}$), V is volume of the chamber headspace above ground surface (cm^3), P_0 is the initial pressure (kPa), S is soil surface area (cm^2), T_0 is initial air temperature ($^{\circ}\text{C}$), R is the universal gas constant, and dC/dt is the initial rate of change in CO₂ mole fraction ($\mu\text{mol}/\text{mol}/\text{s}$).

6.4.3 Typical Data Evaluation Challenges

After review and analysis of CO₂ efflux data, the user may find that the data did not produce results as expected or may be inconsistent with results from other methods. Some items to consider when trying to understand anomalous data include the following.

- Soil moisture changes are more widely varying in shallow soil and may impact ground surface methods more than method implemented deeper in the subsurface such as the gradient method.
- The DCC measurement is a snap shot in time and dynamic conditions such as diurnal fluctuations in temperature and change in weather conditions especially wind and rainfall events, may affect the DCC results.

Any of the above factors can influence the calculation of CO₂ efflux (primarily by over or underestimating the background efflux) and thus NSZD rate at a site. One method to account for background efflux, but still use data from the DCC method, is to use passive flux traps and ¹⁴C correction to measure background at a select few locations.

If data interpretation challenges arise, then the reader is advised to review this section of the document as many of the impacts of these issues are discussed herein. Additionally, the reader is advised to review Section 3 for discussion of key LCSM elements and review inaccuracies in site-specific assumptions that went in NSZD monitoring program design. In most situations, the data can be resolved and useful results obtained after careful data review and optimization of parameters and calculations.

7 Emerging Methods

The NSZD monitoring methods previously described in detail in this document are included because they are published in peer-reviewed literature, are well-developed and have established industry-accepted field and analytical procedures, are gaining acceptance by the regulatory community, and are in widespread onsite use for NSZD monitoring. There are several other methods and method adaptations that have been researched and field implemented, but only on a small scale. Albeit nascent, these emerging methods are reasonable alternative approaches that can be considered on a case-by-case basis for NSZD monitoring programs.

The emerging methods that are discussed in this section include:

- biogenic heat monitoring,
- monitoring of CH₄ efflux, and
- ¹⁴C analysis of vapor samples from probes.

The reader is advised to consider their merits and ability to meet site-specific data needs and consult current literature for more recent advances and method improvements prior to use.

7.1 Biogenic Heat Monitoring

As introduced in 2.2, the oxidation of hydrocarbons is an exothermic reaction. In conjunction with intrinsic microbiological activity, the concurrent presence of petroleum hydrocarbon-impacted soils and permeation of atmospheric O₂ into the subsurface is capable of creating heat within the vadose zone (see Figures 2-3A and 2-3B). At many sites, this NSZD-derived heat generation is significant enough to increase soil temperatures within the vicinity of and above the petroleum hydrocarbon-impacted soils. Current research suggests that NSZD quantification using these thermal signatures in the vadose zone is plausible. Soil temperature increases due to NSZD have been observed and used to quantitatively estimate NSZD rates (Sweeney and Ririe 2014; Warren and Bekins 2015). This is an area of active research because soil temperatures are easy to monitor and they can provide useful, long-term information to evaluate NSZD.

7.1.1 Theoretical Basis

Determining NSZD rates from biogenically generated heat involves two analytical steps, first estimating the heat flux and second estimating the heat from the biodegradation reaction. Each is described in detail below and equations shown to explain how these two analyses are combined to estimate an NSZD rate.

7.1.1.1 Estimating Heat Flux from NSZD

Heat transfer in solids (including soil) occurs by heat conduction, a diffusion-like process that follows Fourier's law (Hillel 1982):

$$G = -K \nabla T \quad (7.1)$$

G is the heat flux ($\text{J/m}^2/\text{s}$), K is the thermal conductivity of the soil ($\text{J/m/s}/^\circ\text{C}$), and ∇T is the temperature (T) gradient ($^\circ\text{C/m}$). If the LNAPL body has a relatively large footprint compared to the LNAPL smear zone thickness, Equation 7.1 can be simplified to a one-dimensional heat flux (G_z) in the vertical direction (z) as:

$$G_z = K_{\text{soil}} \left(\frac{dT}{dz} \right) \quad (7.2)$$

The soil thermal conductivity (K_{soil}) value is the volume-weighted average from all different lithologies in the soil matrix of the oxidation zone where dT/dz is measured. Reported values of the soil thermal conductivity can range from about $0.1 \text{ J/s/m}/^\circ\text{C}$ for dry fine-medium textured soil up to $4 \text{ J/s/m}/^\circ\text{C}$ for water saturated sand and is highly dependent on soil moisture (Hillel 1982; Sweeney and Ririe 2014).

Within the hydrocarbon oxidation zone, microbial processes mediate exothermic reactions that generate stoichiometric amounts of energy. This energy is either used by microbial bacterial populations to grow additional biomass, or it is transferred to the surroundings as heat. If the microbial population is assumed constant (i.e. the LNAPL body is middle- to late-stage [see 2.1.3] and has reached pseudo steady state biomass levels), it can also be assumed that all of the reaction heat is transferred to the surroundings. A simplifying assumption can be made to estimate the heat generated by NSZD processes by assuming that the soil is at a pseudo steady state equilibrium (i.e. constant temperature) and the heat generated from biodegradation is equal to the heat lost to the surrounding soil and groundwater (Sweeney and Ririe 2014). Heat generated within the hydrocarbon oxidation zone can be conducted (dissipated and lost) to zones above and below it. Accordingly, the total heat flux out of the oxidation zone needs to be evaluated at both its upper and lower boundaries (G_u and G_l , respectively). Equation 7.3 presents the theoretical estimate of the NSZD-derived heat flux (G_{NSZD}):

$$G_{\text{NSZD}} = G_u + G_l = -K_u \times \left| \frac{dT}{dz} \right|_u - K_l \times \left| \frac{dT}{dz} \right|_l \quad (7.3)$$

dT/dz is called the thermal gradient. The subscripts u and l correspond to the values at the upper and lower boundaries, respectively, that define the vertical limits of hydrocarbon oxidation.

A schematic control volume for heat generation and transfer is shown in Figure 7-1. The control volume spans the vertical interval of the basal portion of the vadose zone at the top of the hydrocarbon impacted soil (datum) up to the ground surface (*g.s.*). The red shaded depth interval is the hydrocarbon oxidation, or reactive (heat generating), zone where atmospheric O_2 meets underlying hydrocarbon vapors, principally CH_4 . The portion of the control volume beneath the oxidation zone is anaerobic and the portion above is aerobic. Upper (G_u) and lower (G_l) heat fluxes, or losses from the oxidation zone, are shown. A representative, background-corrected, in situ thermal profile is presented to the right of the control volume schematic. With depth as the y axis and temperature as the x axis, it depicts an upwardly increasing thermal gradient on the lower portion of the control volume to illustrate the typical effects of colder underlying groundwater and the warmer oxidation zone. This is where the lower boundary thermal gradient is estimated, as shown in the figure by $\left| \frac{dT}{dz} \right|_l$. In situ temperatures typically reach a peak within the core of the hydrocarbon oxidation zone. Continuing to advance upward and closer to the ground surface and exiting the oxidation zone, the thermal gradient then shifts negative as it approaches a colder ground surface. This is where the upper boundary thermal gradient is estimated, as shown in Figure 7-1 by $\left| \frac{dT}{dz} \right|_u$. Dashed lines on either side and at both ends of the thermal profile are sketched in as a simple means to indicate that fluctuations in groundwater (lower) and ambient (upper) temperatures will affect the in situ temperatures within their close proximity. $\left| \frac{dT}{dz} \right|_u$ and $\left| \frac{dT}{dz} \right|_l$ should be estimated outside of these zones of temperature fluctuation. Doing otherwise will result in measurement error. The thermal gradient should be measured where the temperature profile is linear outside the neighboring zones of ambient fluctuation. Where ambient temperature fluctuations affect the thermal profile of the oxidation zone, background correction is necessary.

NOTE This is a general schematic and only intended to present the concept of subsurface occurrence of NSZD-derived biogenic heat. The magnitude of the thermal signature will vary depending upon site-specific groundwater and ambient temperatures and the nature of the NSZD reactions.

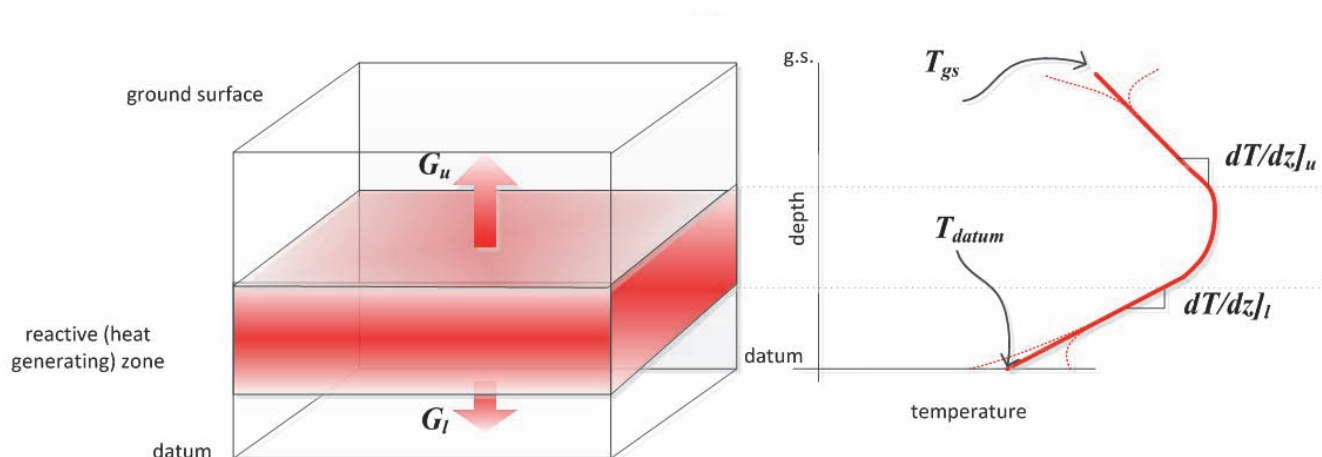


Figure 7-1—Schematic Diagram of NSZD-derived Heat Flux and a Subsurface Thermal Profile

7.1.1.2 Estimating Heat of Reaction from Microbial Activity

A pseudo-steady state heat balance on the control volume in Figure 7-1 also implies that the heat flux from NSZD reactions in the hydrocarbon oxidation zone (G_{NSZD}) is equivalent to the heat generated from microbiological degradation reactions (ΔH_{NSZD} in units of kJ/g) (Warren and Bekins 2015).

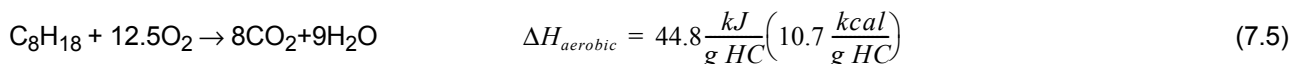
$$G_{NSZD} = \Delta H_{NSZD} \times R_{NSZD} \quad (7.4a)$$

Solving Equation 7.4a for the NSZD rate (R_{NSZD} in units of g/m²/s) results in the following expression:

$$R_{NSZD} = \frac{G_{NSZD}}{\Delta H_{NSZD}} \quad (7.4b)$$

The heat generated from the reactions described by Equations 7.4a and 7.4b can be defined using standard thermodynamic relationships, provided the reaction mechanism is known. The three most prominent reactions within the subsurface include aerobic petroleum hydrocarbon biodegradation, anaerobic petroleum hydrocarbon biodegradation (methanogenesis), and CH₄ oxidation.

Equation 7.5 is a specific example of the biodegradation reaction (and associated heat of reaction, $\Delta H_{aerobic}$ per unit mass of hydrocarbon [HC]) for octane (C₈H₁₈) under aerobic conditions that would be occurring within the upper portion of oxidation (reactive) zone shown in the Figure 7-1 control volume:

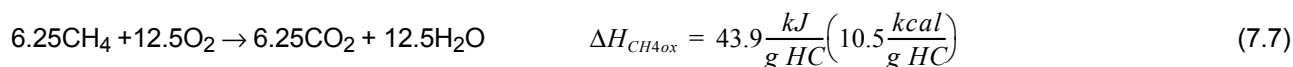


Similarly, Equation 7.6 is a specific example of the biodegradation reaction (and associated heat of reaction, $\Delta H_{methanogenesis}$) for C₈H₁₈ under anaerobic (methanogenic) conditions that would be occurring within the lower portion of oxidation (reaction) zone shown in the Figure 7-1 control volume:



Note that the amount of heat released from aerobic biodegradation is about 50 times higher than that released from anaerobic biodegradation. As a result, the temperature maximum noted in the thermal profile in Figure 7-1 will correspond to the upper portion of the oxidation zone where O₂ is present and aerobic biodegradation is prominent, even when methanogenesis is occurring in the anaerobic zone below it.

Biodegradation of hydrocarbon impacted soil beneath the oxidation zone is anaerobic and forms CH₄. The CH₄ is transported upwards, reacts with O₂ at the base of the oxidation zone (see Figure 7-1), and is oxidized as shown in Equation 7.7:



NOTE The heat of reaction for Equation 7.7 was calculated using 6.25 moles of CH₄ to put it in the same mass basis as that used in Equation 7.6 so that heats of reaction could be directly comparable (i.e. heat generated per gram of hydrocarbon).

As demonstrated by comparison of the heats of reaction in Equations 7.5 ($\Delta H_{\text{aerobic}}$) and 7.7 ($\Delta H_{\text{CH}_4\text{ox}}$), the heat released within the oxidation zone is similar for both aerobic biodegradation of C₈H₁₈ and CH₄ oxidation (44.8 and 43.9 kJ/g HC, respectively). Therefore, for the purposes of approximating biogenic heat mass-based NSZD estimates, sole use of the CH₄ oxidation heat of reaction ($\Delta H = 43.9$ kJ/g HC) is adequate to account for 98 % of the mass of all hydrocarbons (e.g. C₈H₁₈ and CH₄) that are oxidized.

7.1.2 Temperature Measurement Methodology

Temperature measurements in the vadose zone can be made using hand-held probes for a snap shot of temperature conditions at a given time or with dedicated in-place sensors to evaluate changes of temperature over time. Temperature gradients have been estimated by using both probes and sensors placed at different depths in the ground by lowering them to different depths in either special 'water-filled' vadose zone wells (Warren and Bekins 2015), or into existing, atmospherically-sealed groundwater monitoring wells (Sweeney and Ririe 2014).

The vadose zone thermal gradient must typically be "background" corrected to isolate the thermal signature induced by NSZD of the underlying petroleum hydrocarbon-impacted soils. This can be done simply by subtracting the temperatures at the same depths at a location with a similar vadose zone biogeochemical profile that is not impacted by hydrocarbons. The background-corrected thermal gradient can then be used in Equations 7.3 and 7.4b to calculate the rate of NSZD. Warren and Bekins (2015) used this approach to determine a rate of NSZD and were able to verify that the result was consistent with NSZD rates estimated using background-corrected, ground surface, DCC CO₂ efflux measurements.

7.1.3 Limitations of the Biogenic Heat Approach

Use of biogenic heat to estimate NSZD rates has the following limitations, many of which have not been well vetted.

- a) Background correction of the thermal gradient requires that, except for the presence of hydrocarbon impacts, the two locations (impacted and unimpacted) are identical. The thermodynamic effects of deviations such as topographic and water table elevations, lithology, and moisture content have not been fully explored. At a minimum, background measurements should be made at the same time of the year at a location with a similar surface cover, soil stratigraphy, and depth to groundwater.
- b) Equation 7.3 requires that the depth of the top and bottom of the hydrocarbon oxidation zone (as shown on Figure 7-1) be known and the thermal anomaly must align with the zone of O₂ depletion. As CH₄ is readily biodegraded by aerobic microbial soil populations in the presence of O₂, CH₄ oxidation can occur rapidly in a narrow soil band (Davis et al. 2009). As a result, these depths can be difficult to discern. At a minimum, the depth to the temperature maxima must be determined. As discussed in 2.1.3, the location of the hydrocarbon oxidation zone and temperature maxima will vary depending upon various factors including the top elevation of the hydrocarbon impacted soils, soil moisture, and atmospheric exchange of O₂.
- c) There is presently a lack of understanding of the magnitude of downward heat flux due to limited rigorous analysis of temperature measurements in the anaerobic zone above the water table and below the oxidation zone. At some sites the thickness of this zone may be too thin to accurately monitor a downward heat flux. Therefore, to date, the NSZD estimates using the biogenic heat method have been made based on the assumption that the

downward heat flux is negligible. As suggested by Equation 7.3, neglecting this loss results in an estimate that may underestimate the actual NSZD rate if, for example, groundwater is colder than the vadose zone.

- d) Sources of subsurface heat other than hydrocarbon impacted soil can be significant and affect interpretation of subsurface temperatures. Outside sources of heat to consider include site infrastructure such as surface cover and subsurface pipelines, areas of high rates of surface/ground water recharge, and adjacent remediation systems involving aeration (Warren and Bekins 2015). Ideally, thermal monitoring locations are placed outside the zone of influence of these thermal anomalies.
- e) The temperature profile in the vadose zone changes throughout the year due to climatic conditions. Therefore, the biogenic heat data is easiest to interpret in equatorial climates and sites where the depth to the top of the hydrocarbon oxidation zone is greater than 20 ft where subsurface thermal effects due to atmospheric changes are minimal (Sweeney and Ririe 2014). For other sites, temperature monitoring must be performed throughout the year and annual average temperatures used to estimate NSZD rates. This is based on the assumption that due to the cyclical nature of ambient temperatures, the net annual heat exchange between soil and the atmosphere is likely negligible and the pseudo steady state equilibrium (i.e. constant temperature) remains a reasonable assumption.
- f) The specific biological reactions occurring within the hydrocarbon oxidation zone should be known as they are dependent upon local geochemistry. In a rigorous sense, for reactive zones in which multiple reaction mechanisms occur, ΔH_{NSZD} in Equations 7.4a and 7.4b should account for all reaction pathways occurring within the reactive zone. This can be achieved by calculating the reaction extent-weighted average of all reactions. This would require a priori knowledge of the relative extent of each of the multiple reaction mechanisms. In practice however, these equations have only been applied to the aerobic degradation of petroleum (Sweeney and Ririe 2014) and CH_4 (Warren and Bekins 2015). As the heat from CH_4 oxidation and that of aerobic petroleum degradation are nearly equal on a mass basis, a good approximation of the NSZD rate can be obtained without knowing the extent of reaction for each of these biodegradation pathways.

7.2 CH_4 Flux Monitoring

The NSZD quantification methods described in this document are largely based on the assumption that the CH_4 generated by anaerobic biodegradation of petroleum hydrocarbons is completely oxidized by O_2 transported into the vadose zone from the atmosphere. However, sometimes the atmospheric influx of O_2 is insufficient for complete CH_4 oxidation resulting in CH_4 presence in the shallow vadose zone and efflux from ground surface. While this has been demonstrated at two large ethanol fuel spill sites in Minnesota, it is unlikely that CH_4 effluxes will occur at many sites because a unique set of conditions is required for it to occur (Sihota et al. 2013). These conditions include a combination of large CH_4 generation rates, inadequate atmospheric O_2 penetration into low permeability or wet soils, and/or shallow petroleum hydrocarbon-impacted soils.

Although CH_4 flux from the ground surface is typically highly localized to LNAPL source zones, accounting for CH_4 efflux can be an important aspect of quantifying NSZD rates at a site with this condition. In this case, using only the prior described methods, focused on O_2 and/or CO_2 flux, would result in an underestimate of the true NSZD rate. It is important to note that regardless of CH_4 accumulation, N of thSZD is occurring and methods must be adapted to accurately account for it.

Under conditions of parallel occurrence of CO_2 and CH_4 flux through the shallow vadose zone profile above the hydrocarbon impacted soils, the total NSZD rate (R_{NSZD}) can be redefined as:

$$R_{NSZD} = R_{CO_2} + R_{CH_4} \quad (7.8)$$

Where R_{CO_2} is the stoichiometric contribution from CO_2 flux and R_{CH_4} is the contribution from CH_4 flux.

An initial step to evaluate the potential for CH_4 efflux, however, is suggested as discussed in 3.1.3. The additional monitoring could include sampling CH_4 in shallow soil gas (e.g. 2 ft bgs) from a temporary vapor monitoring point

using a field instrument such as an FID. An FID can measure parts per million concentrations of total VOCs and CH₄ with the addition of a carbon filter on the FID probe tip. As an alternative, field analysis of CH₄ can also be performed on a sample collected from a DCC return line after the IRGA finishes its measurement cycle(s). For example, an extra measurement cycle can be added to the DCC program for the sole purposes of allowing time during which the chamber is closed for collection of a vapor sample from the chamber. It is important to note, however, that these additional data will only confirm the presence or absence of CH₄ at or near the ground surface. If efflux or shallow soil gas concentrations of CH₄ are detected, then measurement of the total NSZD rate using Equation 7.8 should be considered.

To account for the presence of CH₄ flux, the field measurements and analytical methods can be adapted. This can be done using both the gradient and DCC methods. Measurement of CH₄ efflux using passive traps could also be performed by modifying the trap design to include an as-yet unidentified CH₄-specific sorbents. To date, this trap adaptation remains conceptual and has not yet been implemented.

7.2.1 CH₄ Flux Monitoring using the Gradient Method

Measurement of CH₄ flux using the gradient method was introduced in Section 4 and is relatively straight forward to perform. In a very similar manner as used for O₂ and CO₂, the vertical concentration gradient of CH₄ in the shallow vadose zone can be estimated using field measurements and graphical analysis. Subsequently, the CH₄ gas flux is estimated using Equation 4.6.

The stoichiometric procedure stated in 3.3.2 to calculate an NSZD rate from the CH₄ flux must then be adapted for methanogenesis using Equation 2.1 (reprinted here):



In this example, to estimate the mass of C₈H₁₈ degraded, the CH₄ flux would be multiplied by the molar ratio of C₈H₁₈ to CH₄ (1/6.25) and multiplied again by the molar weight of C₈H₁₈ (114.23 g/mol).

7.2.2 CH₄ Efflux Monitoring using the DCC Method

The method described in Section 6 of using the DCC to measure CO₂ efflux can be adapted to also quantify CH₄ efflux. It involves use of an atmospheric trace gas analyzer with the DCC soil flux measurement system. Commercial options are available including the Los Gatos Ultraportable Greenhouse Gas Analyzer (Model 915-0011) and Picarro G4301 Analyzer. The real-time, field CH₄ analyzers can be integrated into the closed-loop DCC vapor stream to allow a continuous, flow-through, field analysis of both CH₄ and CO₂ efflux. The CH₄ efflux is then calculated the same way that the CO₂ efflux is calculated by the DCC method.

Similar to the procedure stated for estimating NSZD using the CH₄ flux from the gradient method in 7.2.1, the stoichiometry of Equation 2.1 is then used to estimate the mass of hydrocarbon degraded.

7.3 ¹⁴C Isotopic Correction for the Gradient and DCC Methods

Background correction using the ¹⁴C radiocarbon isotope in conjunction with CO₂ traps to isolate petroleum hydrocarbon biodegradation-derived CO₂ from natural soil respiration was discussed in 5.4.2. While not in routine use, similar ¹⁴C correction methods can be applied to both the gradient and DCC methods.

In the case of the gradient method, soil gas samples can be collected from the vapor probes and analyzed for ¹⁴C using commercially available AMS methods. For example, Sihota and Mayer (2012) describe a method of using ¹⁴C analysis of soil vapor from shallow vapor monitoring probes as a method of background correction for CO₂ efflux values collected using the DCC method. The CO₂ efflux measurement from the DCC was discounted to eliminate the fraction of CO₂ from non-NSZD or natural soil respiration (i.e. modern) sources. In a similar way, the results of the soil vapor ¹⁴C analysis can also be used to correct the CO₂ flux determined using the gradient method.

Because of the ability of isotopic analysis to more definitively quantify NSZD, more widespread use and future methods of using ^{14}C correction are foreseeable. These could include the collection of a smaller sample for ^{14}C analysis using gas-tight syringe directly from the circulating DCC vapor stream or a static chamber. The current limitations that must be overcome before the method could be widely used is the need for a relatively large sample size for AMS analysis. If samples can be collected directly from the DCC or a static chamber, then it would eliminate the need for dedicated vapor monitoring points. However, additional testing is needed to better evaluate the applicability of this approach.

8 Conclusions

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 result in mass losses of LNAPL petroleum hydrocarbon constituents from the subsurface. This document provides practical guidance on NSZD theory, application, measurement methods, and data interpretation.

Since the last NSZD-related guidance was published (ITRC 2009a), significant advances have been made in the methods used to measure NSZD processes, specifically for the vapor phase-related portion of the assessment in the vadose zone. In addition to the gradient method, two new methods have emerged: passive flux trap and DCC. Other methods are also currently being evaluated, making NSZD an active area of environmental research.

This document provides guidance on the use of the three vapor phase-related NSZD quantification methods: gradient, passive flux trap, and DCC, along with providing an overview of emerging approaches. Its main objective is to provide a basis for improved consistency in the application and implementation of NSZD monitoring efforts and evaluation of data. The materials presented in this guidance provide for systematic measurement of NSZD. When coupled with a good LCSM and sound practices by environmental professionals, its use 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.

This document captures the state of the practice and is useful as a guide to develop site-specific plans and evaluate data. 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. The information in this document should be placed into proper context by a project team that is well-versed in site conditions and project data quality and need objectives. The reader is also advised to consult current literature for more recent advances and method improvements.

This guidance is generally applicable to a wide range of environmental remediation sites containing petroleum hydrocarbon impacts in the subsurface. Its use is appropriate at sites that have a need for theoretical, qualitative, or quantitative understanding of vapor phase-related NSZD processes. Because the vapor phase component of NSZD is considered a critical component of an LCSM, this guidance is applicable to most petroleum release sites where risk management and/or remediation is on-going.

8.1 Key Points of Guidance

- NSZD monitoring is applicable to many petroleum impacted sites, while the determination of the rate of NSZD can play a key role in remedial decision making.
- NSZD is most prominently manifested as changes in the vapor phase above the LNAPL footprint; calculating the NSZD rate without considering these gases would result in a significant underestimate of its potential for source mass loss.
- A NSZD monitoring program take can many forms ranging from a simple spot check at a single location in time to determine the potential of NSZD compared to active remediation to monitoring multiple locations site-wide over multi-year increments in time to assess the long-term change in NSZD rates.

- Each monitoring methodology has inherent assumptions that go along with them such as diffusion-controlled transport (gradient method) and complete CH₄ oxidation (passive CO₂ trap and DCC methods). Soil gas monitoring may be conducted to affirm assumptions.
- Understanding key elements of the LCSM as it relates to NSZD is an important first step as it will highlight site conditions which may control/affect NSZD. The LCSM is used as a basis for method selection, monitoring design, and data evaluation.
- Theoretical evaluation of NSZD with a tool as simple as a nomogram can be useful and serve as a basis for expectations and comparison to field measurements.
- Background correction is the largest challenge associated with NSZD monitoring and, therefore, is a key design element for all methodologies that must be tailored to site-specific conditions. All methods require a correction factor to account for non-hydrocarbon derived CO₂.
- Three methods are currently being widely used to monitor NSZD including the gradient, passive flux trap, and DCC techniques. More methods and method adaptations are currently under development and will emerge in the future.
- The gradient method can be applied using existing soil monitoring equipment and offers insight into the soil gas concentration profiles which can aid data interpretation, but depends heavily on reasonable estimates of the effective soil gas diffusion coefficient.
- The passive flux trap method provides a time-integrated, direct CO₂ efflux measurement and can be corrected using ¹⁴C radiocarbon, the most accurate background correction technique currently available.
- The DCC method also provides a direct measurement of CO₂ efflux, but also uses a real-time IRGA technology that can be useful to dynamically map real-time efflux in a higher geospatial density than the other methods.
- Regardless of the method used, soil gas flux measurements are converted to NSZD rates using the same stoichiometric conversion procedure.
- Extrapolation of NSZD rate measurements, typically collected in units of g/m²/d, over large spatial areas and time must be done with careful consideration of the spatial and temporal variability of the data presented using statistical approaches. Extrapolation requires multiple measurement locations and monitoring events, the degree to which depends upon the data use objective.
- NSZD rates vary geospatially and temporally and, in addition, each monitoring method has its own inherent simplifying assumptions and real-world data interpretation challenges. The end result of this compounded uncertainty is a value for NSZD that could be considered an order-of-magnitude estimate. For this reason, results of co-located gas flux measurements using different methods will rarely provide similar results. The practitioner is advised to carefully consider the sources of variability and tailor their NSZD monitoring program objectives and procedures accordingly.

8.2 Future Research Needs

NSZD-related research is ongoing. New techniques and answers to existing questions are either emerging, underway, or being considered. When completed, the results of this new work will enhance and improve NSZD monitoring methods, data quality, and data use.

The following research needs were identified during the writing of this guidance.

- How sustainable are NSZD rates? Do LNAPL mass loss rates decrease as the LNAPL becomes increasingly weathered? Are NSZD rates zero- or first-order? Analysis of long-term (i.e. 20+ years) changes in NSZD rates

and correlation to reductions in petroleum hydrocarbon concentrations in soil will aid in understanding and perhaps support improved estimates of sitewide remediation timeframes.

- Does water table fluctuation or LNAPL submergence impact NSZD rates? Empirical evidence suggests that there is nominal effect on the rate of methanogenesis upon submergence below the water table. However, a controlled study is needed to affirm or dispute the corollary that the NSZD rate is directly related to the rate of methanogenesis and, therefore, independent of water table fluctuation.
- Below the bioactive root zone, what are the effects of natural organic matter (e.g. peat, humic matter) on soil gas profiles, specifically within and above the hydrocarbon oxidation zone? Until better understood, ^{14}C analysis of CO_2 efflux at background locations may be necessary.
- Can a correlation be made between NSZD rates and changes in LNAPL chemical composition?
- What NSZD rate is appropriate for a site that must achieve a regulatory requirement of remediation within a reasonable timeframe? Translation of hydrocarbon NSZD rates into chemical-specific degradation/ remediation rates in soil and groundwater has not yet been approached. It is complicated by NSZD rates that are bulk petroleum hydrocarbon-based and not chemical specific. Integration of NSZD rates, LNAPL composition change, and chemical degradation rates in soil and groundwater may provide some insights into how NSZD data use can be improved and used for remediation performance monitoring purposes.

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Colorado State University Research and Innovation Center
Fort Collins, Colorado

Annex A

(informative)

Example Procedures

The example documents included in this appendix are intended only to show the reader how some project teams implement these procedures. They should not be used without site-specific modifications to adapt them to site conditions, project objectives, and regulatory requirements. It is acceptable to use these procedures as a starting point for site-specific planning.

Appendix A-1

Gradient Method –

Effective Vapor Diffusion Coefficient

Field Test Procedures

APPENDIX A-1

Effective Vapor Diffusion Coefficient Field Test Procedures

A. References

- American Petroleum Institute (API). 2005. *Collecting and Interpreting Soil Gas Samples from the Vadose Zone: A Practical Strategy for Assessing the Subsurface Vapor-to-Indoor Air Migration Pathway at Petroleum Hydrocarbon Sites*. Publication No. 4741. Regulatory Analysis and Scientific Affairs. Washington D.C. November.
- ITRC. 2014. Petroleum Vapor Intrusion – Fundamentals of Screening, Investigation, and Management. Guidance Document PVI-1. Petroleum Vapor Intrusion Team. October. www.itrcweb.org.
- Johnson, P.C., C. Bruce, R.L. Johnson, and M.W. Kemblowski. 1998. "In situ measurement of effective vapor-phase porous medium diffusion coefficients". *Environmental Science and Technology* 32, no. 21: 3405–3409.

B. Purpose and Scope

The purpose is to provide general guidelines for the measurement of vertical soil vapor flux using the gradient method. This procedure assumes that diffusion is the dominant vapor transport mechanism in the soil. Typically, this involves the installation and sampling of multi-depth soil vapor monitoring points, in-situ measurement of effective diffusion coefficients, and calculations based on Fick's Law. This procedure assumes the vapor monitoring points were installed previously and describes the sampling procedures. An example field data form that can be used to record the collected field data is located at the end of this procedure.

C. Equipment and Materials

- 1-liter (L) stainless steel syringe
- 10-milliliter (mL) gas-tight syringe
- Nonreactive tracer gas (e.g., sulfur hexafluoride [SF₆], helium)
- Gas detection device(s) (e.g., SRI GC/ECD for SF₆, MGD-2002 Multi-Gas Detector for helium)
- 1-L Tedlar bags (12 for each location)
- Field logbook

D. Procedures and Guidelines

A. Oxygen Diffusion Coefficient

Estimation of subsurface oxygen diffusion coefficients can be accomplished by using the methods and calculations proposed by Johnson et al. (1998). The field procedure outlined by Johnson et al. (1998) characterizes the effective vapor-phase porous medium diffusion coefficient (D_v^{eff}) within a spherical volume of approximately 9 centimeters (cm) in diameter. This corresponds to approximately a 1-L soil gas volume for a vapor-filled porosity of 0.30 cm³-vapor/cm³-soil.

The general field procedure as described by Johnson et al. (1998) is as follows:

1. Prepare a gas mixture containing approximately 10 parts per million by volume (ppm_v) SF₆ (or other conservative tracer gas such as helium at detectable concentrations).
2. Inject 5 mL of 1 ppm_v SF₆ into a 1-L Tedlar bag containing 1-L of SF₆-free air.

3. Measure the resulting concentration in the 1-L Tedlar bag (should be approximately 5 parts per billion by volume [ppb_v]); record and denote this value as C_{max} .
4. Inject 5 mL of 1 ppm_v SF₆ into the desired location in the vadose zone through small-diameter tubing (1/8-inch stainless steel tubing is preferred). Follow this injection with sufficient SF₆-free air to ensure that the 5 mL of SF₆ has just been flushed from the tubing into the vadose zone (it is desired that the total injected volume be minimized; approximately 1 mL/ft for 304 SS 1/8-inch tubing with 2.1 mm i.d.).
5. Immediately withdraw enough soil gas to fill a 1-L Tedlar bag. Analyze and record the SF₆ concentration in the 1-L Tedlar bag.
6. Inject 5-10-L of clean air into the vadose zone at this sampling before conducting a longer test.
7. Repeat steps 4, 5, and 6 except wait for periods of 15, 60, and 120 minutes before withdrawing the soil gas sample for analysis.
8. Reduce the data by dividing the measured concentrations by C_{max} (this is equivalent to determining η , the fraction of mass recovered).

Once the field protocol is completed, the theory and equations outlined in Johnson et al. (1998) can be used to calculate the effective vapor-phase porous medium diffusion coefficient. With a relatively simple change in the multiplier, this procedure can be adapted to estimate the diffusion coefficient of any gas of interest for natural source zone depletion (NSZD) monitoring including oxygen, carbon dioxide, and methane.

E. Acronyms and Abbreviations

cm	centimeter
cm ³	cubic centimeters
L	liter
mL	milliliter
mm	millimeter
NSZD	natural source zone depletion
ppb _v	parts per billion by volume
ppm _v	parts per million by volume
SF ₆	sulfur hexafluoride

Sheet ____ of ____

Exterior Soil Gas Probe Sampling Log

Project Information			
Project Name:		Project # :	
Sampler Name:		Date/Time:	
Site Information			
Site Name:			
Address:			
<u>Site Information:</u>			
Describe ground cover:			
Depth to groundwater (feet below ground surface):			
Describe vadose zone soil type(s):			
Was a soil boring log completed? Was a probe diagram completed?			
Soil Gas Probe As-Built, Leak Checking, Purging, & Sampling Log			
Probe Location ID (describe and show on a diagram)		Landfill Gas Meter Information	
Sample Identification (Field ID)		Make, Model and S/N -	
Probe As-Built Information		Calibration Standards -	
Date Installed		FID-VOC Monitor Information	
Depth of Borehole (feet below ground surface)		VOC Meter Make, Model,	
Bottom of Probe Screen (feet below ground surface)		Calibration Standards -	
Length of Probe Screen (inches)		Field Analysis Results	
Diameter of Probe Screen (inches)		O ₂ (%)	
Dead Volume - including screen, sand pack, and tubing (mL)		Date: CO ₂ (%)	
Manifold Leak Check	Leak Check Results - Sample Manifold (Pass/No Pass)	Time: CH ₄ (%)	
Probe Leak Check*	Leak Check Results (% or ppmv helium)	N ₂ (%)	
Probe Purge	Pump Purge Rate (mL/min)	FID-VOC Filtered (ppmv)	
	Purge Start Time	FID-VOC Unfiltered (ppmv)	
	Purge Vacuum (" Hg)	Field Analysis Results	
	Purge Completion Time	O ₂ (%)	
*The soil gas probe passes the helium leak check if the detected helium concentration is less than 1,000 ppm (0.1%). Do NOT collect a soil gas sample if the probe fails the helium leak test.		Date: CO ₂ (%)	
		Time: CH ₄ (%)	
		N ₂ (%)	
		FID-VOC Filtered (ppmv)	
		FID-VOC Unfiltered (ppmv)	

Weather Conditions during Sampling:

Observations and Comments:

REV. 10/12/16

Field Personnel:

Calibration and Results:

[illegible]

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Appendix A-2

Dynamic Closed Chamber Procedures

APPENDIX A-2

Dynamic Closed Chamber (DCC) Efflux Measurement and Data Handling Procedures

A. References

LI-COR Biosciences. 2005. LI-8100 Automated Soil CO₂ Flux System Instruction Manual.

LI-COR Biosciences. 2012. LI-8100A Automated Soil CO₂ Flux System – Field Guide.

B. Installation Procedures

Installation procedures for soil collars in non-frozen and frozen ground are included in **Attachment 1** and **2**, respectively. Ground surface preparation procedures for installation of soil collars in especially hard or compacted soil is included in **Attachment 1**.

Following installation of the soil collars, soil in the area of the collar are recorded and photographed. Before measurements begin, the offset (height of the collar top lip above ground surface) is measured. This measurement is used to estimate the total volume of air inside the chamber and collar and is an important part of the overall efflux calculation. An average value of the offset measured from three sides of the collar are used to estimate it as accurately as possible. An example field data form that can be used to record the collected field data is located at the end of this procedure.

C. Measurement Procedures

1. Install the soil collar.
2. Set up the measurement. The LI-COR controller is set up with the following parameters:
 - a) Chamber Offset = Average collar height above soil
 - b) Observation Delay = 0 seconds
 - c) Deadband = 20 seconds
 - d) Observation Rate = 90 seconds
 - e) Post-purge = 30 seconds
 - f) Minimum Number of Measurements = 3
3. Place the chamber over the collar.
4. Start the measurement. Enter file name (location ID) and any site-specific comments.
5. Transfer files to a computer.
6. Import the data into the computer program SoilFluxPro to evaluate the computation and data reduction.

D. Measurement Description

The control unit automatically operates the chamber bellows, pump, and infrared CO₂ gas analyzer (IRGA) unit to perform efflux measurements. The pump and IRGA start and initiate a short period of pre-measurement purge. All cycles are controlled using user-definable timers. Following the purge cycle, the bellows is inflated to close the chamber tight atop the collar. The pump circulates vapor through the chamber and back into the analyzer unit for CO₂, temperature, and water vapor measurement. The IRGA measures the change in CO₂ concentrations in the vapor return line connected to the chamber.

After a short deadband period, which is the time interval set to allow steady mixing in the chamber after it closes, the analyzer records the change in CO₂ over time until the pre-set measurement period ends. The water and temperature data are used to correct the measured CO₂ to a dry standard unit of measure. After the measurement period ends, the bellows deflates, the chamber is raised off the collar, and a post-measurement purge cycle is initiated. This process of bellows inflation, measurement, and bellows deflation continues until the preset number of measurements are collected at each location. The control unit then stops all function and allows the user to view the data and evaluate whether additional measurements are needed at the same location or whether measurement is complete. When measurements are complete, the user lifts the chamber and analyzer units, and moves to the next location to repeat the process.

E. Quality Assurance / Quality Control

Appropriate quality assurance and quality control measures are essential to assess the accuracy and precision of the data collected. Although detailed and robust calibration is completed by most manufacturers of dynamic closed chamber (DCC) systems under controlled laboratory settings, a span calibration of the instrument in the field is recommended prior to collecting field efflux data. Typically, this involves calibration to a 0-parts per million (ppm) CO₂ standard and a span gas with a 500-ppm CO₂ concentration.

A minimum of one duplicate efflux monitoring location per every 10 locations is recommended. The duplicate collar should be installed the same way as the original location and placed no more than approximately 3 feet from the original location, in similar ground cover. Basic statistics including the calculation of a relative percent difference (RPD) from the natural and duplicate sample data are performed to assess data quality. An RPD greater than 30 percent may prompt the user to assess the soil collar installation procedures to ensure a good seal with the subsurface was attained.

Additionally, a field blank is collected during each field event by attaching a closed collar that does not allow gas flow into the chamber. A total of 60 readings are obtained for each field blank.

F. Recordkeeping

An example field data form that can be used to record the collected field data is located at the end of this procedure. Some of the more important fields on the sampling sheet template include: soil collar installation details (including installation method, date, and weather conditions during installation), calibration results and setup details of the DCC instrument, and measurement data that include date/time, location, average offset measured from three points on the collar, ground cover details, flux measurement and trace gas concentrations. Documentation of weather conditions is also very important and recorded prior to the start of each measurement at an individual location.

G. Data Handling

Data QA/QC, analysis, and reduction should be performed at the end of each week that CO₂ data have been collected. If it is the first time you have analyzed LICOR data, you will need to download LI-8100A Instrument Software v3.0.1 for free from <http://www.licor.com/env/support/>. Save this onto your desktop.

1. Open LI-8100 File Viewer 3.1.0 (the program downloaded from above).
2. Open all files collected from the field that require attention. You will be given the option to merge them all in the one view, but suggest not to at this point – thus click “No.”
3. Go to – View > Display Variables. Select:

a. Label	c. Offset	e. IV Pressure
b. IV Date	d. Vtotal	f. IV H ₂ O

g. IV Cdry	o. Post-Pruge	w. IV CO2ABS
h. Exp_dCdry/dt	p. IRGA Averaging	x. IV H2OABS
i. IV Tcham	q. Virga	y. IV RAWCO2
j. Area	r. Vcham	z. IV RAWCO2REF
k. Exp_Flux	s. Exp_FluxCV	aa. IV RAWH2O
l. Obs#	t. Exp_R2	bb. IVRAWH2OREF
m. Observation Length	u. Exp_Co	
n. Observation Delay	v. IV CO2	

Save these parameters (click on the floppy disk symbol). This should save all parameters so they should automatically be shown each time you open LI-8100 File Viewer 3.1.0.

4. Double click on the first line of information. Another window will appear.
5. Select the "Regression Analysis" tab.
6. Ensure that 1st order is not selected , if it is then deselect it.
7. If the R2 (curve fit) value for the Expon is close to 1, no edits will need making. If it is <0.95 the start time will need altering to correct for this. More than likely the start time will need delaying until the "curve" becomes less variable. Change time and press "compute."
8. If any changes are made and they increase the R2 value be sure to select "Keep." If they do not increase R2 select "Revert,"
9. Do this with every line of information on every tab. As all the information is checked on each tab the tab may be closed, be sure to save the data file with an updated name. Do not overwrite files.
10. Once all files have been checked, R2 values made more accurate, and the files saved under an updated name, re-open all files only this time merge them into one view.
11. Ensure all parameters previously mentioned are present.
12. Next export the data. File > Export, select "same as view" and export.
13. Save the text file in the same place that the original files so all data are kept in the same place.
14. Once the data are in a text file open excel and the text file.
15. Select all data in the text file and then copy and paste them into the Excel file in order to import the data in the correct format.
16. Save the excel table to the same location as the original files.
17. Add columns at the end of the table
 - a. Surface cover
 - b. Pressure Average
 - c. Temperature Average
 - d. CO2 Efflux Average
 - e. Standard Deviation
 - f. % of Average
18. If Exp_Flux values are between 0 micro-mole per meter squared per second ($\mu\text{mol}/\text{m}^2/\text{s}$) and -0.2 $\mu\text{mol}/\text{m}^2/\text{s}$ considered equal to 0 $\mu\text{mol}/\text{m}^2/\text{s}$ in the CO2 Average Efflux calculation.
19. If the efflux value is less than -0.2 $\mu\text{mol}/\text{m}^2/\text{s}$ do not use.
20. If the R2 value is less than 0.50 do not use.
21. Refer to the LICOR data field work sheets, if any comments have been made suggesting data not be used, or mentioning instrumental or field errors do not use data.

22. Move all unused data to an additional table at the bottom of the existing table titled "Eliminated Data."

List the reasons above for eliminating data next to the table and highlight, where possible, the reason for elimination.

Attachment 1

Ground Surface Preparation Procedures

Ground Surface Preparation Procedures – Soil Collar/Receiver Pipe

A. Purpose and Scope

The purpose is to provide general guidelines for the compaction of soils in and around the soil vapor efflux measurement pipe and soil collars associated with carbon dioxide (CO₂) efflux measurement systems such as passive flux traps and the DCC soil flux system. This procedure is strictly related to the placement and re-compaction of soil removed as part of the pipe and collar installation into the shallow ground surface (i.e., less than 4 inches depth). An example field data form that can be used to record the collected field data is located at the end of this procedure.

B. References

LI-COR Biosciences. 2005. LI-8100 Automated Soil CO₂ Flux System Instruction Manual.

LI-COR Biosciences. 2012. LI-8100A Automated Soil CO₂ Flux System – Field Guide.

Appendix A-3, Passive Flux Trap Field Procedures

C. Equipment and Materials

- Hand trowel
- 3-inch curved carpet knife
- 5-gallon bucket(s) and/or plastic sheeting for soil storage
- Kevlar or cut-resistant gloves
- ASTM D-698 Standard Proctor Compaction Hammer (5.5 lbs. with 12-inch drop)
- Field logbook

D. Procedures and Guidelines

A. Excavation and Preparation for Backfilling

It is generally preferred to directly push the pipe and collar into the ground. This can be performed using manual or hammer means. However, some more difficult soil conditions require a concurrent method of soil removal (excavation) and direct push. The following guidelines are provided to support a higher quality installation using either direct push or excavation means.

1. If soil is saturated, pipe/ collar should not be installed and soil must be allowed to drain/ dry out after a rain event prior to installation.
2. Manually remove surface and shallow vegetation from installation location to minimize background CO₂ influence. If roots are encountered during excavation, remove and discard them.
3. During shallow excavation activities to accommodate the insertion of the soil vapor efflux measurement pipe/collar, excess soils removed should be placed in a 5-gallon bucket or on plastic sheeting adjacent to the work area. This is done to segregate the soil removed in order to only replace the soils that were removed initially.

4. Following insertion of the pipe or collar, and prior to backfilling, the field personnel should measure the depth from the ground surface to the bottom of the pipe (i.e., the depth of the excavation).
5. If the excavation depth exceeds 4 inches, the backfilling will require placement of two separate soil lifts of equivalent thickness (e.g., if the excavation is 6 inches deep, the backfill is replaced and compacted in two separate 3-inch-thick lifts).
6. All large particles (i.e., anything 3 inches or larger in diameter) should be set aside and not replaced in the excavation. Large particles such as rocks, will inhibit the ability to adequately compact smaller soil particles and may result in nesting or voids below these larger particles. Additional smaller particulate materials may be gathered from surrounding soil for replacement, if required.
7. If, during initial excavation, it is determined that greater than 50 percent of the soil removed consists of large particles (i.e., those particles greater than 3 inches in diameter), AND those conditions appear to match the surrounding soil conditions, all materials should be selectively replaced in lifts to match the thickness of the largest particle and compacted per instructions provided below.
8. During removal, if soils are mostly clay/silt, it will be important to break up clods larger than 2 inches in diameter before materials are backfilled. This can be done by use of the hand trowel in the 5-gallon bucket or on the plastic sheet.

B. Backfilling and Compaction

Once the soil vapor efflux measurement pipe or collar has been installed using either direct push or excavation means, the process of replacing the soils within the area inside and outside the pipe or collar can begin and those soils can be compacted to closely match the surrounding soil conditions based on the field observations.

1. Using the hand trowel, replace the soil from the 5-gallon bucket or the plastic sheeting in an even horizontal loose lift to the maximum allowable thickness indicated in Section A above across the entire area (i.e., both inside the pipe and outside the pipe).
2. Begin compaction of the inside of the pipe first. Start in the center. Place the hammer sleeve in the center of the pipe with the hammer resting on the ground. Firmly hold the sleeve in-place and lift the hammer (via the ball on the top) to maximum height (12 inches) and allow the hammer to free fall. Lift the sleeve and note the amount of indentation to the soil surface in the field book. Move carefully around the initial compaction spot by systematically moving the sleeve to an adjacent uncompacted spot and repeating the hammer drop gradually moving toward the pipe sidewall. Continue moving the sleeve and dropping the hammer until the entire surface area of the soil inside the pipe has been compacted with one hammer blow.
3. Move to the disturbed soil outside of the pipe. Start at the outside sidewall of the pipe, repeat the compaction process described in Step 2 moving around the pipe first and covering the area toward the outside edge of disturbed soil. Continue until the entire area of disturbed soil outside of the pipe has been compacted with one hammer blow.
4. Move back to the center of the pipe and only perform one hammer drop at that location. Do not continue to compact soils inside pipe at this time. After the hammer drop, stop and note the amount of indentation to the surface in the field book.
5. Move to an area outside of the area that was previously excavated (an area of undisturbed soil), but contains soils that are similar to those in the excavated area. Perform one hammer

drop on the ground surface in the undisturbed area and note the amount of indentation to the ground surface in the field book.

6. If the indentations from Step 4 and Step 5 are equal or the indentation in Step 4 is less than the indentation in Step 5, no further compaction of the soil inside the pipe and the disturbed soil outside the pipe is necessary and the second loose lift of soil (if required) can be placed and compacted per Step 2.
7. If the indentation in Step 4 is greater than the indentation in Step 5, repeat Step 2 on the same lift both inside and outside the pipe. When completed, repeat Step 4 and compare to the indentation recorded for Step 5.
8. Upon replacement of all soils from the 5-gallon bucket and/or plastic sheeting, the backfilling process is considered complete. No additional soils should be added.

The primary function is to replace the soils in and around the pipe to closely match the surrounding in-place soils. This SOP focuses on lift thickness placement (i.e., a thin level lift that is placed loose) and the number of tamps used to compact the soils to closely match the surrounding soil conditions.

E. Key Checks and Preventative Measures

- Keep 5-gallon bucket(s) and/or plastic sheeting close to excavation area to avoid long reach and limit repetitive bending at the waist.
- If using only plastic sheeting, be sure to segregate soil piles from separate pipe locations and note which pipe location goes with which soil pile. Similarly, the 5-gallon bucket should be used for only one pipe excavation at a time. Do not comingle excavation soils in one bucket.
- After each pipe installation, be sure to stand and stretch. Avoid repetitive bending for periods longer than one round of compaction work.
- Keep the working space clean with plastic sheeting and good housekeeping.
- Maintain field equipment in accordance with the manufacturer's recommendations.
- This will include, but is not limited to:
 - Inspect compaction hammer and replace as warranted
 - Inspect excavation devices and replace as warranted

Attachment 2

Frozen Ground DCC Collar Installation Procedures

Frozen Ground DCC Collar Installation Procedures

A. Purpose

To install PVC collars for the collection of efflux measurements using the LI-COR 8100A carbon dioxide (CO₂) soil flux system including the flux chamber and infrared gas analyzer (IRGA) where soil conditions are frozen and impenetrable to the standard collar installation method.

B. References

LI-COR Biosciences. 2005. LI-8100 Automated Soil CO₂ Flux System Instruction Manual.

LI-COR Biosciences. 2012. LI-8100A Automated Soil CO₂ Flux System – Field Guide.

C. Frequency

One collar per sample location installed 12 to 24 hours before data collection, where possible.

D. Location

Perform this procedure at designated sampling locations as stated in the work plan. Sampling should encompass locations above contamination and background locations away from contamination. All ground surface covers should be included in background and contaminated locations, i.e., gravel, grass, organic, etc.

E. Materials

- 8-inch-diameter Schedule 40 PVC collar designed for LI-COR 8100A survey
- 2-inch by 4-inch $\frac{3}{4}$ -inch thick plywood
- Rubber mallet
- Shovel or small trowel for digging
- Tamping device
- Wetted cloth (or equal) to form an impermeable seal around the LI-COR flux chamber on the plywood

F. Preparation and Precautions

- Clear all snow and ice from sampling location
- Clear all vegetation from the sampling location

G. Procedures

- Place the collar on the ground, and insert as far as you are able using hand tools.
- For solid frozen surfaces, simply score a shallow (<1 cm) rut in which the collar can sit.
- For field temperatures consistently sub-zero (**Figure 1**) - Place a wet (not dripping) cloth (J-cloth) around the base of the outside of the collar. Try to ensure that water from the cloth does not run into the inside of the collar.

- After the cloth freezes and sets around the collar, pour a small amount of water on it to form a continuous ice seal all the way around the collar. Ensure all gaps between the ground and collar are filled and let the cloth freeze.

H. Quality Assurance and Corrective Action

- Collection photo documentation of each collar location and review historical documentation to ensure that the locations are consistent and/or are as expected.
- Do not perform field monitoring if the temperature falls below -20 °C. The unit is not rated for lower temperatures.
- If it snows after the collar is installed, remove as much as possible from the collar prior to completing data collection
- If vegetation happens to collect in the collar after installation, remove prior to completing data collection
- **Before collecting data ensure the IRGA is up to temperature.** It will collect data when it is not up to temperature, but it will be no good. A red light bulb will illuminate on the control panel when the IRGA reaches its proper temperature set-point, do not proceed until it is lit.

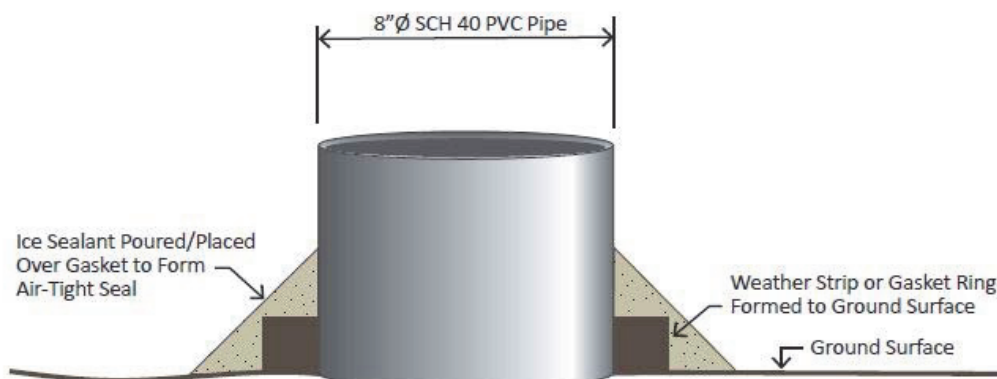


Figure 1 – Below-zero Degrees Celsius Collar Installation

Sheet ____ of ____

Dynamic Closed Chamber Quality Assurance/Control Log

Project Information							
Project Name:		Project # :					
Field Technician Name:		Date/Time:					
Site Information							
Site Name:							
Address:							
DCC Survey Information:							
Describe survey scope:							
Number of survey locations:							
Describe type(s) of ground cover:							
DCC System Calibration and Blank Run Log							
DCC System Information		Make, Model and S/N - Calibration Standards and Results - <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 30%; padding: 5px;">Calibration Gases</td> <td style="padding: 5px;">Zero Gas Specifications</td> </tr> <tr> <td style="padding: 5px;"></td> <td style="padding: 5px;">CO₂ Gas Specification</td> </tr> </table>		Calibration Gases	Zero Gas Specifications		CO ₂ Gas Specification
Calibration Gases	Zero Gas Specifications						
	CO ₂ Gas Specification						
DCC Blank No. 1	Blank Collar Offset (cm)	DCC Blank No. 3	Blank Collar Offset (cm)				
Date:	Observation Delay (sec)	Date:	Observation Delay (sec)				
Time:	Observation Rate (min:sec)	Time:	Observation Rate (min:sec)				
	No. of Observations		No. of Observations				
	Average CO ₂ Efflux (μmol/m ² /s)		Average CO ₂ Efflux (μmol/m ² /s)				
	Measurement Comments		Measurement Comments				
DCC Blank No. 2	Blank Collar Offset (cm)	DCC Blank No. 4	Blank Collar Offset (cm)				
Date:	Observation Delay (sec)	Date:	Observation Delay (sec)				
Time:	Observation Rate (min:sec)	Time:	Observation Rate (min:sec)				
	No. of Observations		No. of Observations				
	Average CO ₂ Efflux (μmol/m ² /s)		Average CO ₂ Efflux (μmol/m ² /s)				
	Measurement Comments		Measurement Comments				

Weather Conditions:

Observations and Comments:

REV. 11/21/16

Soil CO₂ Efflux Measurements
Dynamic Closed Chamber Method Measurement Field Log

Site Name and Location: Location ID: Page ____ of ____

Project Number: Date:

Project Manager and Phone Number:

Field Personnel:

Soil Collar Installation Details

Date Installed: Offset (cm):

Installation Method: Ground Cover and Soil Conditions:

Observation Delay (sec):

Observation Rate (min:sec):

Measurement Results							Measurement Comments
Date/ Time of Collection	New/Appending Data File	Obs. #	Current Weather Conditions	Unfiltered FID-VOC (ppmv)	Filtered FID-VOC (ppmv)	CO ₂ Flux (μmol/m ² /s)	

Observations and Comments:

Appendix A-3

Passive Flux Trap Field Procedures



EoFLUX

SOP

**STANDARD OPERATING
PROCEDURE:
CO₂ TRAP DEPLOYMENT
AND REPLACEMENT
PROTOCOL**

For questions contact:

Julio Zimbron, Ph.D.
E-Flux, LLC
3185-A Rampart Road, Room 250D
Fort Collins, CO 80521
o: (970) 492 4360 c: (970) 219-2401
jzimbron@soilgasflux.com

Last modified: July 13, 2015.

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INTRODUCTION

The following document describes protocols for deployment of CO₂ traps in support of studies to evaluate rates of natural attenuation of light non-aqueous phase liquid hydrocarbons (LNAPL). The document includes a list of tools required for deploying the traps. Material Safety Data Sheets (MSDSs) for the sorbent media in the traps, and the lubricant to be used on the receiver ends are available upon request.

The traps are filled with a proprietary non-hazardous CO₂ sorbent, consisting of a mixture of calcium and sodium hydroxides (strong bases). Thus, caution should be used when handling traps. The sorbent media is contained within the traps and should not pose a direct contact hazard as long as the traps are not damaged and are handled with care. Personal protective equipment selection for handling the media is defined in the MSDSs. As a minimum, the use of nitrile gloves beneath leather work gloves and safety glasses when handling the fully assembled traps is recommended.

EQUIPMENT LIST

- 1) SOP (this document), MSDS sheets for CO₂ Sorbent and and lubricant gel.
- 2) Site maps.
- 3) CO₂ trap shipment and installation log – will be shipped with traps from E-Flux.
- 4) Appropriate PPE (not provided, to be determined by site contractor).
- 5) CO₂ trap receivers– to be installed at the site previous to first trap deployment. Receivers will stay at the site until last planned sampling event is complete.
- 6) CO₂ trap rain covers.
- 7) CO₂ Traps– Will be shipped to the Site by E-Flux.
- 8) Diffusion cap– These should remain onsite between sampling rounds.
- 9) Flathead screwdriver, or nut driver tool (Not provided) to remove ring clamp from top rubber shipping cap.
- 10) Temperature Loggers (optional).

NOTE: All shipments include a contents list. If shipment contents do not match list, do not proceed to installation and contact E-Flux immediately.

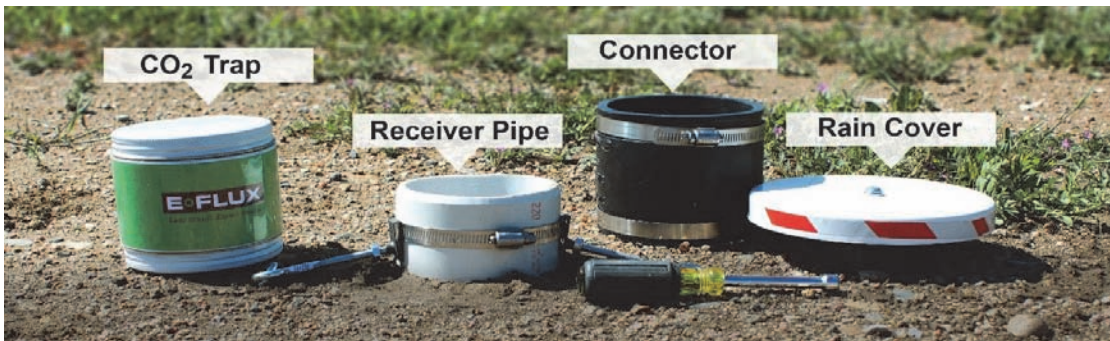


Figure 1. CO₂ trap (shown capped), receiver pipe, connector and rain cover.

GENERAL PLACEMENT GUIDELINES

- It is recommended that trap locations are near existing groundwater monitoring wells. This is important for data discussion and correlation of CO₂ fluxes to known geologic, hydrogeologic, and hydrocarbon distribution conditions.
- Suitable trap locations require soils that are permeable to gas transport. Pavement or low permeability surface covers (including free standing water, ice, or extremely compacted soils) should be avoided.
- In some sites, variability within close locations due to soil heterogeneity can be large. If testing for variability, replicate traps should be located within 10 feet of each other.
- Excess surface vegetation should be cleared from directly beneath the proposed trap location prior to installation of the in-ground receiver.
- If desired, background locations (unimpacted) should be chosen where soils, vegetation, and general site conditions are similar to the LNAPL monitoring locations.
- Additional site data that might be useful for data discussion includes:
 1. Groundwater temperatures. Due to the exothermic nature of biodegradation, in some cases groundwater temperatures have correlated to biodegradation rates estimated based on soil gas fluxes (McCoy, et al, 2014).
 2. Soil gas concentration profiles at discrete vadose zone locations or in well headspace (Wilson et al, 2013) might reveal high CO₂ and/or methane concentrations and thus be indicative of areas of high rates of LNAPL degradation.
 3. Groundwater and LNAPL levels in wells (if applicable).

IN-GROUND RECEIVER INSTALLATION

This section describes the standard operating procedure, suitable for temporary monitoring points in most uncompacted soils. If soils are compacted and/or monitoring locations are intended to be permanent (i.e., for long term monitoring), users should review accompanying document "Guideline for Alternative In-Ground Receiver Installation for Long Term Monitoring and/or Compacted Soils". For standard In-Ground Receiver Installation:

- 1) Ensure that vegetation is removed from the trap installation location.
- 2) Tighten the eye screws through the U-nuts placed on the receiver
- 3) Place receiver in ground. Keeping the receiver vertical push the receiver using a rubber mallet and the provided direct push tool.
- 4) Hammer the stakes through the eye screws on a 45° angle.
- 5) Compact soil to achieve compaction as close as possible to pre-installation conditions.



Figure 2. In-ground Receiver Installation (Steps 2-5)

RECOMMENDATIONS FOR DEPLOYMENT

- To avoid trap saturation or non-detectable measurements (due to extreme high or low CO₂ fluxes, respectively), field traps shall be deployed as determined during project planning. A typical deployment period of 2-weeks is sufficient for most common CO₂ flux ranges of interest.
- One Trip Blank is included with each batch of traps. This trap should not be opened. It will remain at the Site and must be returned to E-Flux with the other traps after the sampling Period.
- **KEEP TRAPS UPRIGHT.**
- **Traps contain caustic material, use caution when handling.** Avoid unnecessary shaking or abrupt movements.
- Sorbing material is moisture resistant, but not water proof. **Keep traps dry and avoid unnecessary moisture.**

TRAP DEPLOYMENT PROCEDURE

A shipment and installation chain of custody (COC) form (field log) will be shipped with the traps. The COC should be filled out with the date and time that each trap is installed and removed for return. A period of one day is recommended between installation of the receiver pipe and trap deployment, to allow for soil equilibration after disturbance.

- 1) Find the appropriate trap for the location (ref. site map).
- 2) **Carefully** slide connector onto the installed receiver pipe. Using a flat head screwdriver tighten the bottom clamp.
- 3) Unscrew top and bottom caps off the CO₂ Trap (set caps aside as these will be needed for shipping the traps back to E-Flux).
- 4) Screw rain cover onto the top side of the CO₂ Trap (keep trap upright).
- 5) **Carefully** slide CO₂ Trap into the connector. Using a flat head screwdriver tighten the top clamp on the connector.
- 6) Place Identification label on the connector.



Figure 3. In-ground Receiver Installation (Steps 1,3,4,6-8).

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SOP: Receiver Pipe Installation Guide

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Page 6

RETURNING TRAPS TO E-FLUX

- 1) At end of monitoring period, reverse steps. Place a small amount of lubricant on the PVC shipping plug before inserting back into bottom of the trap. The bottom cap (PVC) should slide in the bottom of the trap with relatively little effort. The top cap (rubber) should be put after the bottom one. Note date and time removed from ground on the log. Place the log in dry cooler with traps. The traps have stored the CO₂ in a stable form (as carbonates)- the best way of handing them is by keeping the traps dry. Other means of preservation (such as ice or refrigeration) are not necessary (nor desirable).
- 2) Ship to E-FLux in dry coolers. Keep traps upright. Notify E-Flux of tracking number after shipping to the following address:

E-Flux, LLC
Julio Zimbron, Ph.D.
3185-A Rampart Road, Room D257
Fort Collins, CO 80521
office: (970) 492-4360 cell: (970) 219-2401
Attn: Julio Zimbron
Email: jzimbron@soilgasflux.com

Annex B (informative)

Case Study of Three NSZD Estimation Methods

A case study of natural source zone depletion (NSZD) monitoring is presented to illustrate how the API NSZD guidance can be applied. To cover the breadth of the guidance content, it contains details ranging from site conditions to an analysis of results. Although some of the details are fictional, it is largely based on a real setting where NSZD monitoring was performed. Table B-1 presents the information that this case study seeks to provide.

Table B-1—Summary of Key Content in the Case Study

Content	Section, Table, or Figure No.
Description of site conditions of key relevance to design of an NSZD monitoring program	Sections B.1.2 and B.1.3
Presentation of an example work scope that includes elements of all three NSZD monitoring methods highlighted in this document	Sections B.1 and B.2
Summary of field procedures for all three methods used to measure the NSZD rates and supplemental data collection used to further characterize site conditions	Section B.2
Tabular and graphical presentation of data collected during the monitoring program	Tables B-3, B-6, and B-7 and Figures B-3 through B-6 and B-10
Discussion of field measurement and data evaluation challenges	Section B.3
Example use of nomograms and calculations to demonstrate use of equations presented in the API NSZD guidance	Sections B.3.1.1 through B.3.1.3 and B.3.3
Detailed discussion of results from each method and location	Section B.3
Comparative analysis of NSZD estimates from the various methods and explanation of differences	Table B-5 and Section B.3.5

B.1 Introduction

Three NSZD estimation methods were applied at a petroleum products terminal. The gradient, passive flux trap, and dynamic closed chamber (DCC) methods were each applied at multiple locations at the site to evaluate the distribution and rates of NSZD. The results of the methods are compared, and factors that may contribute to variability and uncertainty are discussed.

This was an NSZD research study and three NSZD monitoring methods were applied for the purpose of demonstration and comparison. While multiple lines of evidence are often useful for assessing NSZD, this case study does not imply that three methods must be used at all sites. Section 3.1.5 of this document addresses method selection based on site-specific data objectives and needs.

B.1.1 Objectives

The three methods used a diverse range of approaches to measure the flux of gas derived from subsurface NSZD processes. The gradient method applies Fick's First Law by using effective soil vapor diffusion coefficients combined with field analyses of soil gas concentrations (oxygen [O₂], carbon dioxide [CO₂], methane [CH₄], and volatile petroleum hydrocarbons) from nested wells at different depths. The passive flux method uses laboratory analysis of sorbent in CO₂ traps deployed at the ground surface that sequester CO₂ over a multi-week period. The DCC method uses a closed-loop circulation of soil vapor between a chamber and an IRGA to measure instantaneous CO₂ flux at the soil surface.

The objectives of the study were to estimate the NSZD rates across the site and compare NSZD rates estimated by each methodology under the same site conditions.

B.1.2 Site Background

The site is a 20 acre active petroleum products terminal located in a subtropical climate in the southern United States that has been in operation since the 1950s. Petroleum products are conveyed to the site via underground pipeline, stored in aboveground tanks, and loaded into tanker trucks for subsequent transport and sale. Field activities were conducted in five areas of the site, shown on Figures B-1 and B-2 and summarized in Table B-2.

Shallow groundwater at the site occurs within an interval of silty to sandy clay soils with few variations in color or texture that extends from the ground surface to at least 100 ft bgs (Figure B-2). The NSZD assessment focused on the upper portion of the shallow aquifer system, where light non-aqueous phase liquid (LNAPL) has been observed. Groundwater is typically first encountered at depths from 15 to 20 ft bgs. Seasonal variations in depth to groundwater are typically ± 2 ft. Regional water levels have gradually declined 5 to 10 ft over the past 20 years due to groundwater extraction.

Table B-2—Summary of Measurement Methods and Locations

Sampling Location	Soil Gas Sampling for Gradient Method	Effective Diffusion Coefficient Testing	Barometric/Soil Gas Pressure Differential	Passive CO ₂ Trap Deployment	DCC Measurement
NSZD-1	•	•		•	
NSZD-2	•	•		•	•
NSZD-3	•	•	•	•	•
NSZD-4	•	•		•	•
Background			•	•	•

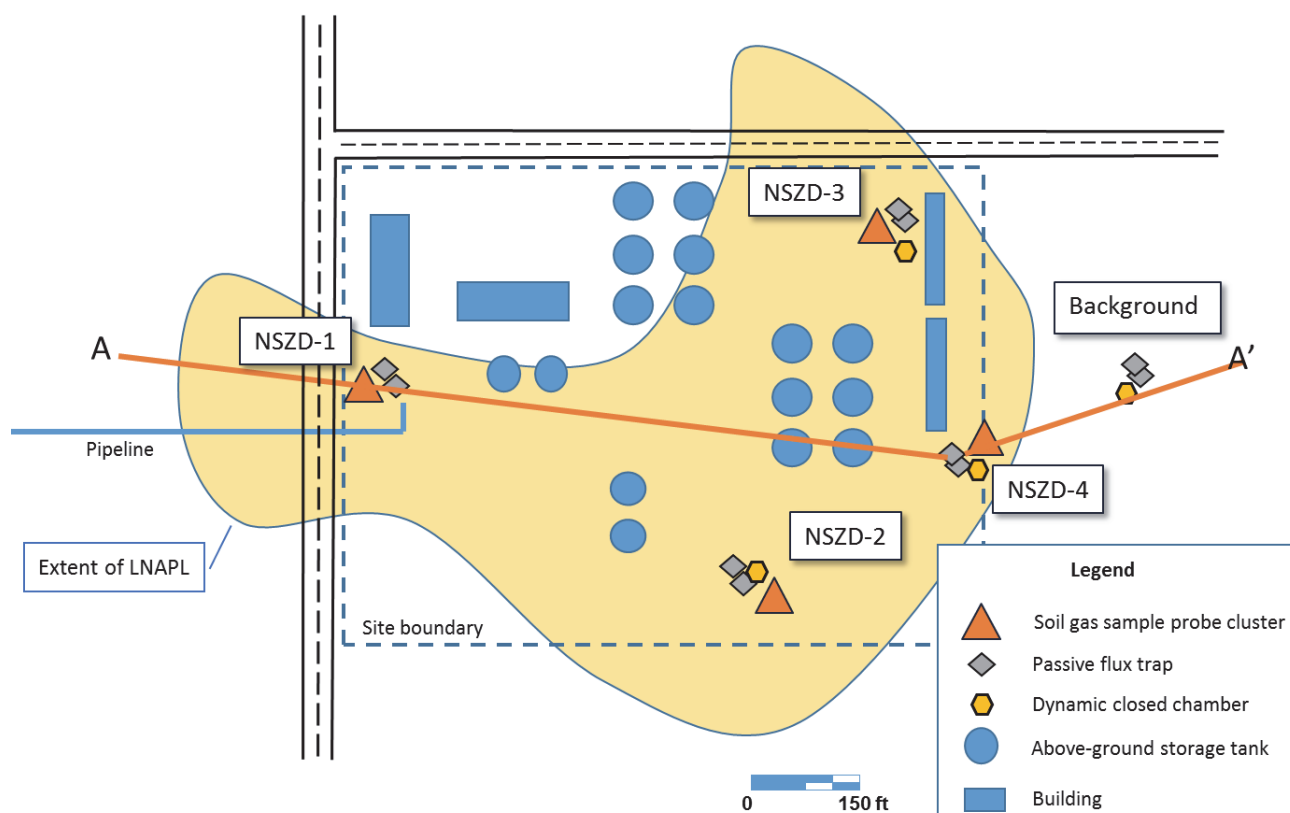


Figure B-1—Site Layout and Locations of NSZD Monitoring

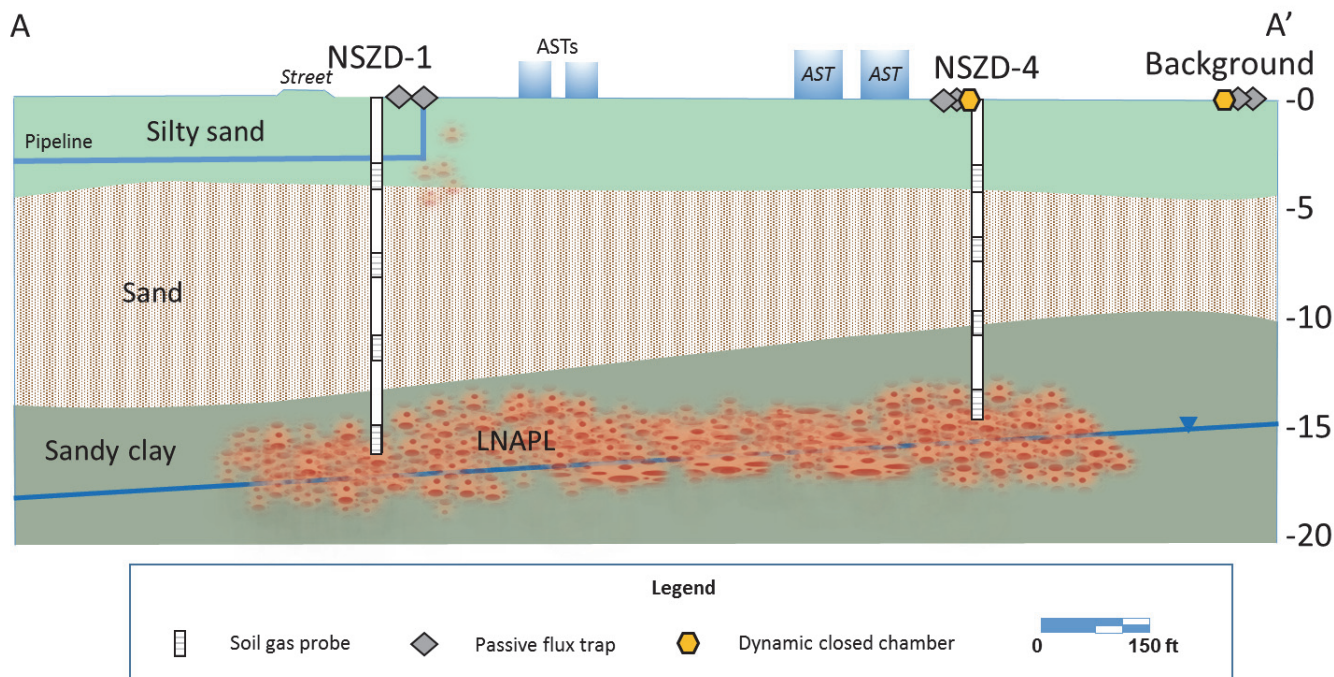


Figure B-2—Cross Section A-A'—Soil Texture, LNAPL Occurrence, and NSZD Monitoring Locations

B.1.3 LNAPL Occurrence

Multiple sets of characterization data were previously compiled at the site to estimate the horizontal and vertical extent of LNAPL in soil. The data included laboratory analyses of soil samples, hand-held soil headspace photoionization detector (PID) measurements collected during drilling, stains and odors observed during drilling, measurements of LNAPL in monitoring wells, and the use of a direct-push probe fitted with a laser-induced fluorescence (LIF) sensor.

The most frequent and extensive occurrences of LNAPL were observed near the tank farm areas; the approximate horizontal and vertical extent of the LNAPL is shown in Figures B-1 and B-2. The coincidence of the manifold pipeline and tank farm areas to locations where LNAPL was recorded in borings and monitoring wells suggests that releases from these site features may be the primary sources of LNAPL in the subsurface. The vertical extent of LNAPL-impacted soil varies across the site, occurring generally between 12 and 20 ft bgs.

Compositional analyses of LNAPL indicate a mix of gasoline, diesel, and jet fuel, in variable proportions and degrees of weathering.

B.2 Field Methodology

Three NSZD estimation methods were applied at four nested soil gas sample probe clusters. NSZD-1 through NSZD-4 were installed to measure soil gas concentrations within the LNAPL plume footprint. The probes were constructed of 1/4 in. outside diameter Nylaflo® tubing with a 6 in. long stainless steel screen at the end depth. Each cluster consisted of four depth-discrete sampling probes, distributed from approximately 4 ft bgs to slightly above the average water table, which ranged from 12.5 to 16 ft bgs. Soil gas samples were collected and effective diffusion coefficient tests were performed using procedures consistent with Section 4 and Appendix A. A background location was not employed for this application of the gradient method due to economic reasons.

B.2.1 Soil Gas Sampling and In Situ Soil Vapor Diffusivity Testing for the Gradient Method

Prior to collection of each sample, a negative-pressure leak test was conducted on the sampling train. Additionally, a helium leak test was also performed on each sample probe. Results of the field tests and analytical data indicated no significant leaks in the sampling train and all helium detections were within specifications.

Soil gas samples were collected into Tedlar® bags using the vacuum box method and field-screened with a landfill gas analyzer to measure concentrations of CH₄, O₂, and CO₂ using a Landtec GEM™2000. Samples could not be collected at the two deepest probes at NSZD-4 because the sampling probes appeared to be blocked or submerged.

Samples were shipped to a laboratory and analyzed for fixed gases (nitrogen [N₂], O₂, CO₂, and CH₄) by ASTM Method D1946 and TPH by U.S. EPA Method TO-15. Because elevated CH₄ concentrations had been observed during field screening, gas samples were shipped in accordance with USDOT and the IATA requirements for Class 2 hazardous materials.

Soil gas sampling results are summarized in Table B-3 along with estimated concentrations of fixed gases at the soil surface (zero depth) that were assumed to be at standard atmospheric conditions.

Following collection of soil gas samples, in situ soil vapor diffusivity testing was conducted at each of the 11 sampled soil gas probes using the tracer gas sulfur hexafluoride (SF₆). The tests were conducted according to the procedures outlined in Johnson et al. (1998) and described in 4.3.

Table B-3—Soil Gas Sampling Results

Location	Depth ft bgs	Gasoline Range Organics (GRO) (mg/m ³)	Carbon Dioxide (% v/v)	Methane (% v/v)	Oxygen (% v/v)	Nitrogen (% v/v)	Helium (% v/v)
All ^a	0	0	0.04	0.0002	20.9	78.1	0.0005
NSZD-1	4	23,500	7.9	6.7	8.9	71.9	0.49
	8	43,800	8.9	10.9	8.1	67.9	0.50
	12	78,200	13.6	21.5	1.6	57.6	0.13
	16	109,000	15.9	40.4	0.6	36.8	0.06
NSZD-2	3.5	1,020	6.4	0.4	6.0	77.0	0.30
	6.5	24,700	15.5	29.8	1.4	49.0	0.18
	9.5	55,000	15.2	34.2	0.5	44.0	ND
	12.5	120,000	18.4	36.5	0.3	42.0	ND

Table B-3—Soil Gas Sampling Results (Continued)

Location	Depth ft bgs	Gasoline Range Organics (GRO) (mg/m ³)	Carbon Dioxide (% v/v)	Methane (% v/v)	Oxygen (% v/v)	Nitrogen (% v/v)	Helium (% v/v)
NSZD-3	4	3.0	12.2	0.11	10.0	79.4	0.22
	7	1,030	13.9	1.9	0.5	78.0	ND
	11	2,070	13.7	14.0	0.6	63.0	0.09
	15	109,000	19.1	25.0	0.3	53.0	ND
NSZD-4	4	5.5	8.4	0.02	10.4	78.3	0.39
	7	860	8.7	52.1	3.3	27.6	0.45
	10	Sample could not be collected					
	13	Sample could not be collected					
^a Concentrations estimated using standard atmospheric composition.							
NOTE bgs = below ground surface mg/m ³ = milligram per cubic meter % v/v = percent by volume ND = Not detected							

B.2.2 Passive Flux Trap Deployment

Five areas were targeted for CO₂ trap deployment, including four locations adjacent to the existing soil gas probe clusters where the gradient method was applied (NSZD-1 through NSZD-4), and a Background location in an area outside of the LNAPL footprint (see Figure B-1). Passive CO₂ traps were provided and analyzed by E-Flux, LLC (Fort Collins, Colorado). Although trap locations were targeted to be near the soil gas sampling clusters, actual locations were adjusted to avoid paved areas, foundations, or other structures that could affect soil gas flow. Soil gas sampling location NSZD-4 is in a paved area outside of the site fence; the trap location was shifted approximately 10 ft to a nearby unpaved, grassy area within the site perimeter. All other CO₂ traps were located on unvegetated gravelly open ground.

For all locations, paired duplicate CO₂ traps were deployed, approximately 5 ft apart, to evaluate measurement reproducibility.

Passive flux trap installation, deployment, and retrieval procedures were consistent with those presented in Section 5 and Appendix A.

B.2.3 DCC System Implementation

CO₂ flux was also measured with the DCC method using two LI-8100A long-term, automated soil flux systems provided by LI-COR, Inc. (Lincoln, Nebraska). The DCC was installed at four locations (NSZD-2 through NSZD-4 and Background) and were co-located with the passive CO₂ traps (see Figure B-1). The Background location is outside of the known LNAPL footprint. The DCC units were programmed to collect one CO₂ flux measurement per hour for 16 days. The procedures used for the DCC system were consistent with those described in Section 6 and Appendix A.

Multiple deployment issues were encountered with the DCC unit. At NSZD-3, the DCC stopped recording data after 3 days, apparently due to failure of the deep-cycle battery and subsequent loss of power. The marine battery was replaced and the unit was moved to a new location near NSZD-2. Unfortunately, the unit continued to function poorly, and detailed review of the data indicated that usable flux measurements were not collected at the NSZD-2 location.

Follow-up troubleshooting efforts with the manufacturer after return of the unit indicated that a faulty or worn electrical connection within the unit caused these issues.

The other DCC unit, which was deployed at NSZD-4 and the Background location, was observed to reduce the data collection frequency near the end of each measurement period. This was caused by an undersized solar panel that could not recharge the battery at a rate sufficient to keep pace with power consumption. Data quality was not compromised, however, and the DCC unit exhibited consistent measurement performance and collected an extensive set of viable data.

B.2.4 Supplemental Data Collection

In addition to assessment of NSZD rates, supplemental data were collected to explore the potential influence of subsurface pressures on NSZD processes. Pressure transducers were used to characterize differential pressure between atmospheric air and soil gas. The methods used along with details of the field implementation are described below.

B.2.4.1 Barometric and Soil Gas Pressure Data

To evaluate the potential for soil gas flow (advection), two soil gas pressure transducers were deployed during the NSZD assessment period. Each transducer was programmed to record pressure at 15 minute intervals throughout the study. One transducer was deployed in a background location open to the atmosphere, and the second was connected to the 11 ft deep soil gas sampling probe at NSZD-3.

B.2.4.2 Weather Station Data

To supplement the on-site data collected during the study, ambient temperature and barometric pressure data were retrieved from a nearby airport, and daily precipitation data were retrieved from a weather station in a nearby town located within one mile of the site.

B.3 Results and Discussion

Three NSZD estimation methods were applied at the site and the results from each are discussed below, followed by a relative comparison. The results are discussed in detail to highlight important aspects of data collection and interpretation. As this study was performed for demonstration and study purposes, the data analysis herein is relatively rigorous. Data interpretation is a site-specific activity to meet specific data objectives and its rigor should be considered on a case-by-case basis.

B.3.1 Gradient Method Results

B.3.1.1 Soil Gas Concentration Profiles

Table B-3 presents a summary of the raw data and Figures B-3 through B-6 present the soil gas concentration profiles for NSZD-1 through NSZD-4, respectively. The soil gas profiles generally provide evidence that NSZD is occurring. The results are consistent with general expectations of O₂ and CO₂ exhibiting opposing (mirror image) trends with depth. In general, the figures show that CH₄ is produced near the hydrocarbon-impacted soil interface consistent with the presence of anaerobic biodegradation, and O₂ is consumed and CO₂ is produced consistent with the expected process of aerobic biodegradation and hydrocarbon oxidation in the overlying formation. The presence of volatile petroleum hydrocarbons (i.e. gasoline-range organics [GRO]) in soil gas, concentrations increasing with depth, also indicates that volatilization and degradation of the LNAPL are occurring.

The profiles also generally show that CH₄ is generated in the saturated zone and is offgassing into the vadose zone and displacing N₂, as observed by the depleted N₂ concentration, and the relatively constant volumetric sum of CH₄ and N₂ at each depth.

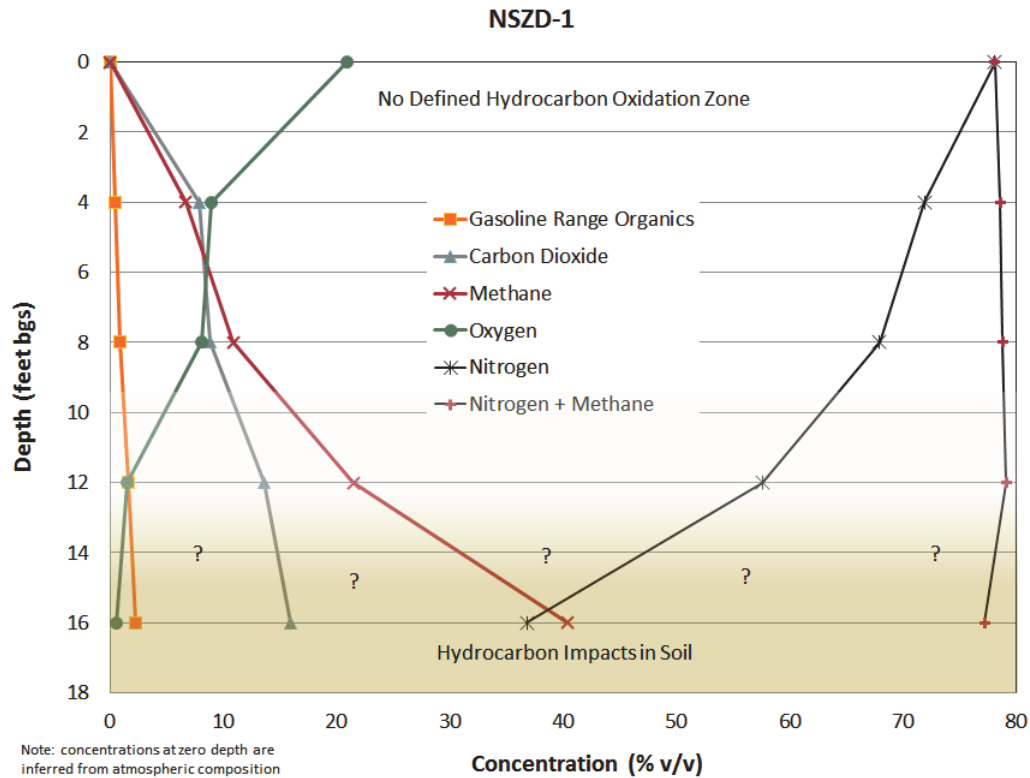


Figure B-3—Soil Gas Concentration Depth Profile at NSZD-1

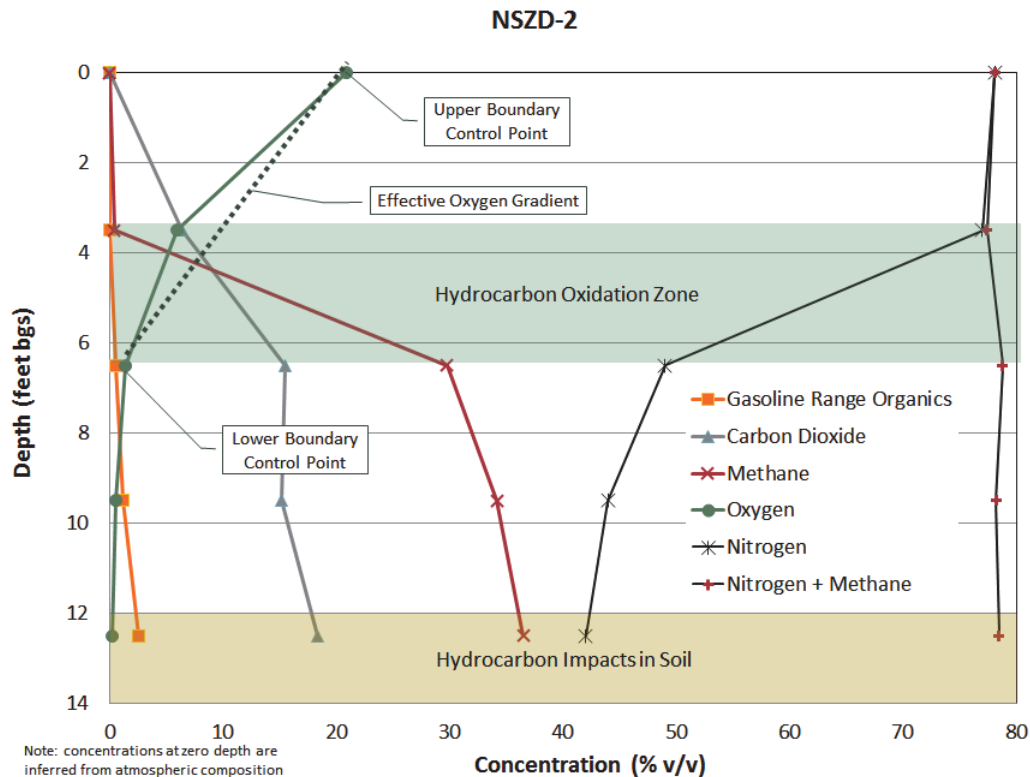


Figure B-4—Soil Gas Concentration Depth Profile at NSZD-2

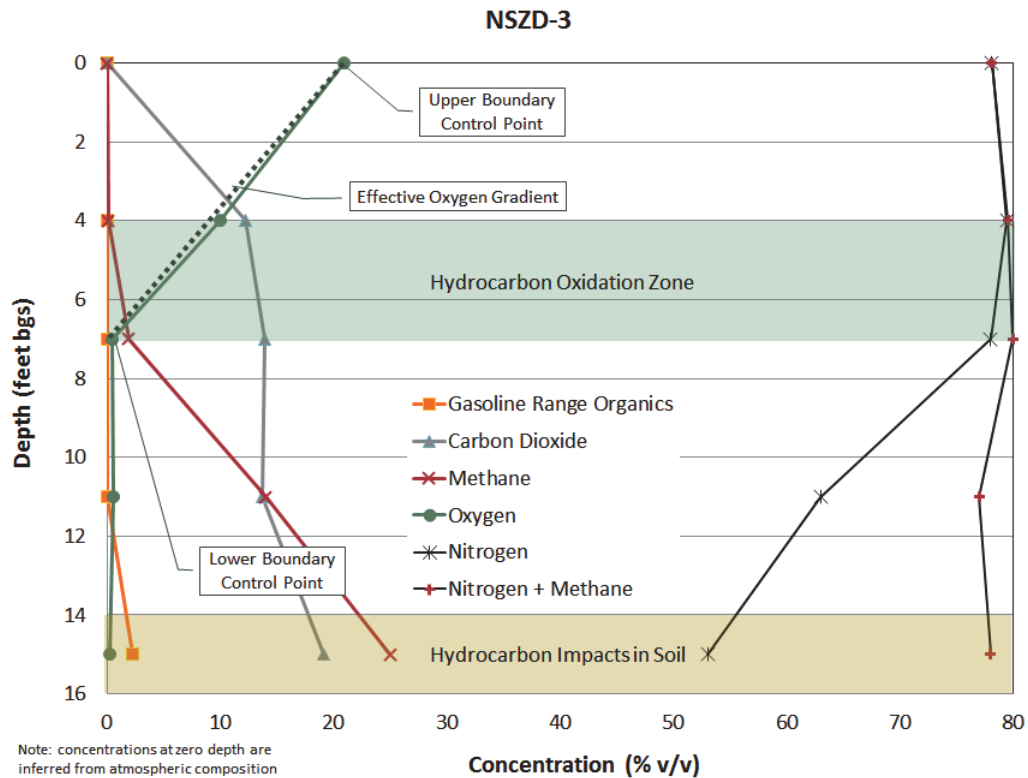


Figure B-5—Soil Gas Concentration Depth Profile at NSZD-3

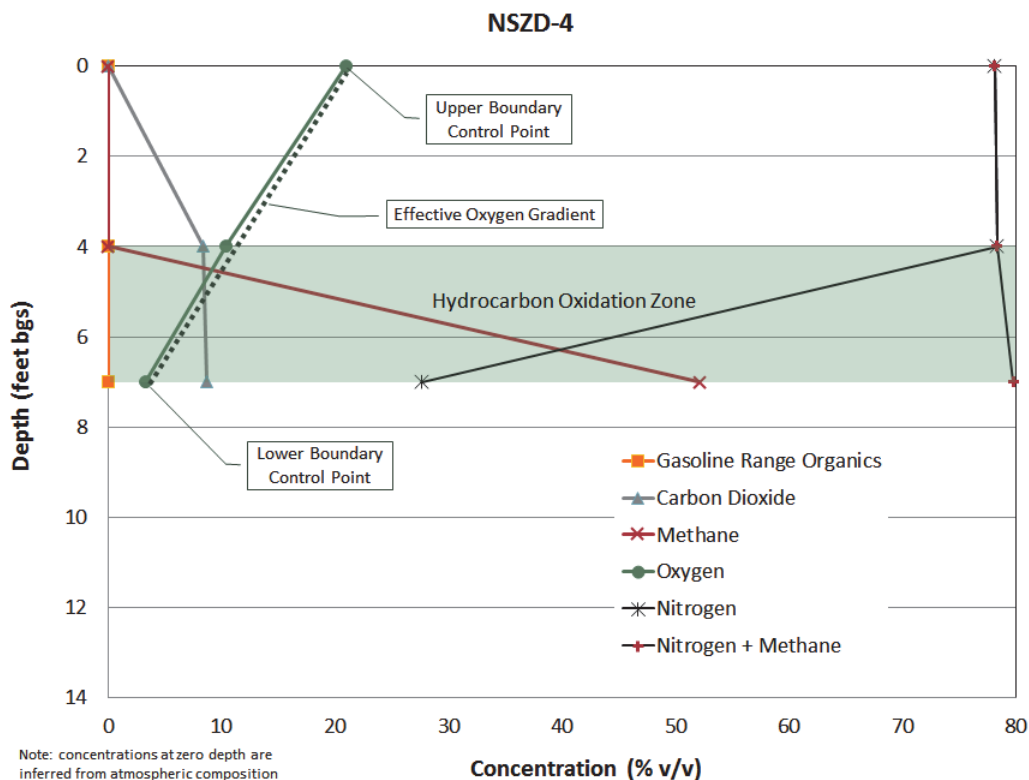


Figure B-6—Soil Gas Concentration Depth Profile at NSZD-4

The soil gas data for NSZD-2 and NSZD-3 (see Figures B-4 and B-5, respectively) show the following.

- O_2 , which is consumed during aerobic biodegradation of hydrocarbons and CH_4 , was present at concentrations less than atmospheric conditions at all subsurface locations, with a significant decrease from 3 to 7 ft bgs.
- CO_2 , a byproduct of aerobic biodegradation of hydrocarbons and CH_4 , was greater than atmospheric conditions at all subsurface locations, with a significant increase between 3 to 7 ft bgs.
- In general, the hydrocarbon oxidation zone at locations NSZD-2 and NSZD-3 appears to occur between the two shallowest soil gas sampling probes (3 to 7 ft bgs).
- CH_4 concentrations were low in shallow samples and increased with depth, indicating that methanogenesis is occurring in and near the saturated zone. CH_4 is then transferred to and through the vadose zone via offgassing and ebullition, where it is subsequently oxidized.
- Volatile non- CH_4 hydrocarbons (GRO) were detected in deeper soil gas, indicating that LNAPL is also being depleted via direct volatilization. The concentrations decrease several orders of magnitude closer to ground surface and indicate that it is also being aerobically biodegraded in the vadose zone along with the CH_4 .

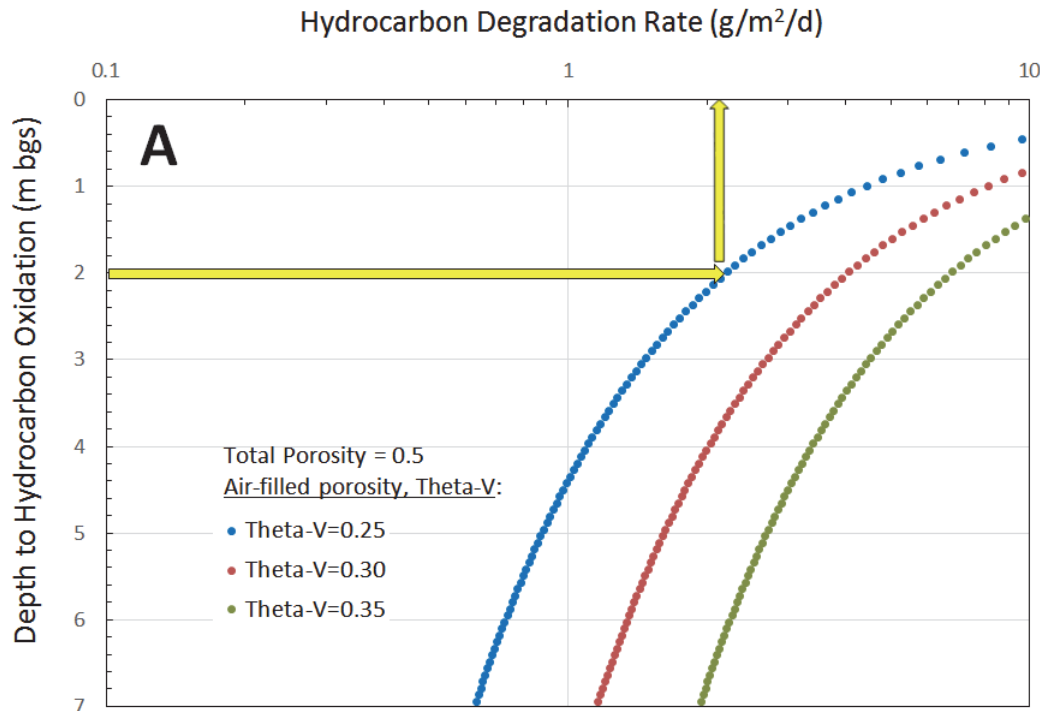
In contrast, the soil gas profile at NSZD-1 (see Figure B-3) differed significantly from NSZD-2 and NSZD-3. The shallowest soil gas sample probe at 4 ft bgs had depleted but detectable O_2 , elevated CO_2 , detectable GRO hydrocarbons, and elevated CH_4 . These data suggest the presence of nearby shallow hydrocarbon-impacted soil (such as a nearby surface release), or restricted soil gas exchange, or both. The land surface near LNAPL-1 is gravel covered with no vegetation. However, NSZD-1 is near a pipeline manifold where at least one historical release has occurred, thus the presence of shallow impacted soil is hypothesized near this location. The presence of significant CH_4 in the shallowest soil gas sample also suggests the potential for CH_4 efflux from ground surface. These results do not conclusively indicate that CH_4 and other hydrocarbons are discharging to the atmosphere, as complete hydrocarbon oxidation may be occurring at very shallow depths (i.e., within a few inches of ground surface). However, because they only measure the CO_2 efflux, it suggests the potential for low bias in NSZD estimates from the passive flux trap and DCC methods at these locations. Section 7.2 discusses procedures to address this shortcoming in the methods. In addition, the hydrocarbon oxidation zone was judged to be poorly defined, and the anomalous co-occurrence of O_2 and CH_4 at 4 ft bgs is questionable; therefore, gradient method calculations were also not performed for location NSZD-1.

At NSZD-4 (see Figure B-6), GRO hydrocarbon and CH_4 concentrations at the shallowest soil gas sampling interval (4 feet bgs) were low (GRO 5.5 mg/m³ and CH_4 0.02 %), while O_2 was partially depleted (10.4 %) and CO_2 was elevated (8.4 %). This pattern is potentially indicative of shallow soil respiration dominated by natural organic matter, which, without background correction, could bias the apparent NSZD rate. Further (yet still incomplete) O_2 depletion was observed in the next depth interval (7 ft bgs, 3.3 %). With full CH_4 depletion occurring between 4 and 7 ft bgs, and no evidence of CH_4 surface emissions, the position of the hydrocarbon oxidation zone was conservatively estimated to be near 7 ft bgs.

With relatively well-defined O_2 depletion depths at NSZD-2 and NSZD-3, a screening-level estimate of the NSZD rate can be obtained using the nomograms discussed in 3.1.4.1. The apparent depth to O_2 depletion at the hydrocarbon oxidation zone at either of these locations is at most 6.5 to 7 ft (2 m). The air-filled porosity of the shallow unsaturated soils is roughly 0.25. Using the nomogram in Figure 3-1A, repeated here as Figure B-7, a 2 m depth to oxidation and an air-filled porosity of 0.25 corresponds to an approximate hydrocarbon degradation rate of about 2 g/m²/d.

B.3.1.2 Effective Diffusion Coefficient for Oxygen

Site-specific effective diffusion coefficients for O_2 were calculated from the SF_6 tests at the four soil gas sampling clusters (NSZD-1 through NSZD-4). The SF_6 tracer gas was prepared and injected at each of the soil probes using the procedures in Appendix A. Samples were withdrawn at periods of 15, 60, and 120 minutes for analysis, and the



(adapted from Ririe and Sweeney, 2016)

Figure B-7—Estimated Hydrocarbon Degradation Rate Using Depth and Porosity

measured concentrations were divided by the initial concentration $C_{\max}$ to obtain the equivalent of η , the fraction of mass recovered. The equations presented in 4.3.1 were used to estimate the diffusion coefficients.

The calculated O_2 effective diffusion coefficients ranged from $0.025 \text{ cm}^2/\text{s}$ at 16 ft bgs to $0.012 \text{ cm}^2/\text{s}$ at 4 ft bgs at NSZD-1. This variability is consistent with the observed heterogeneity and fining downward from silty clay to sandy clay soil in the vadose zone and are generally consistent with literature values (Johnson et al. 1998; ITRC 2009). Diffusion coefficients for the shallowest depth interval in each cluster are shown in Table B-4. As discussed in more detail below, these were used for the gradient method O_2 flux calculations.

Table B-4—Oxygen Effective Diffusion Coefficients

Depth (ft bgs)	$D_{\text{eff}}, \text{O}_2 \text{ (cm}^2/\text{s)}$			
	NSZD-1	NSZD-2	NSZD-3	NSZD-4
4	0.012	0.0084	0.0060	0.0042
7 - 8	0.0033	0.0086	0.0056	0.0065
11 - 12	0.0033	-	0.0050	-
15 - 16	0.0025	-	-	-
Average	0.0038	0.0085	0.0059	0.0047
NOTE $D_{\text{eff}}, \text{O}_2$ = effective soil vapor diffusion coefficient for oxygen cm^2/s = square centimeter per second				

As discussed in 3.1.4.1, the hydrocarbon degradation rate can also be estimated from the effective O_2 diffusion coefficient and the apparent depth to O_2 depletion. The effective O_2 diffusion coefficient in the upper 7 m of NSZD-2

and NSZD-3 ranges from 0.0056 to 0.0086. Selecting an intermediate value of 0.007 and using the nomogram in Figure 3-1B, repeated here as Figure B-8, and a 2 m depth to zero O_2 concentration, correspond to an approximate hydrocarbon degradation rate of $2.5 \text{ g/m}^2/\text{d}$. Combining the screening results and use of the two nomograms (Figures B-7 and B-8), the expected range of NSZD rates at this site would generally range from 2.0 to $2.5 \text{ g/m}^2/\text{d}$.

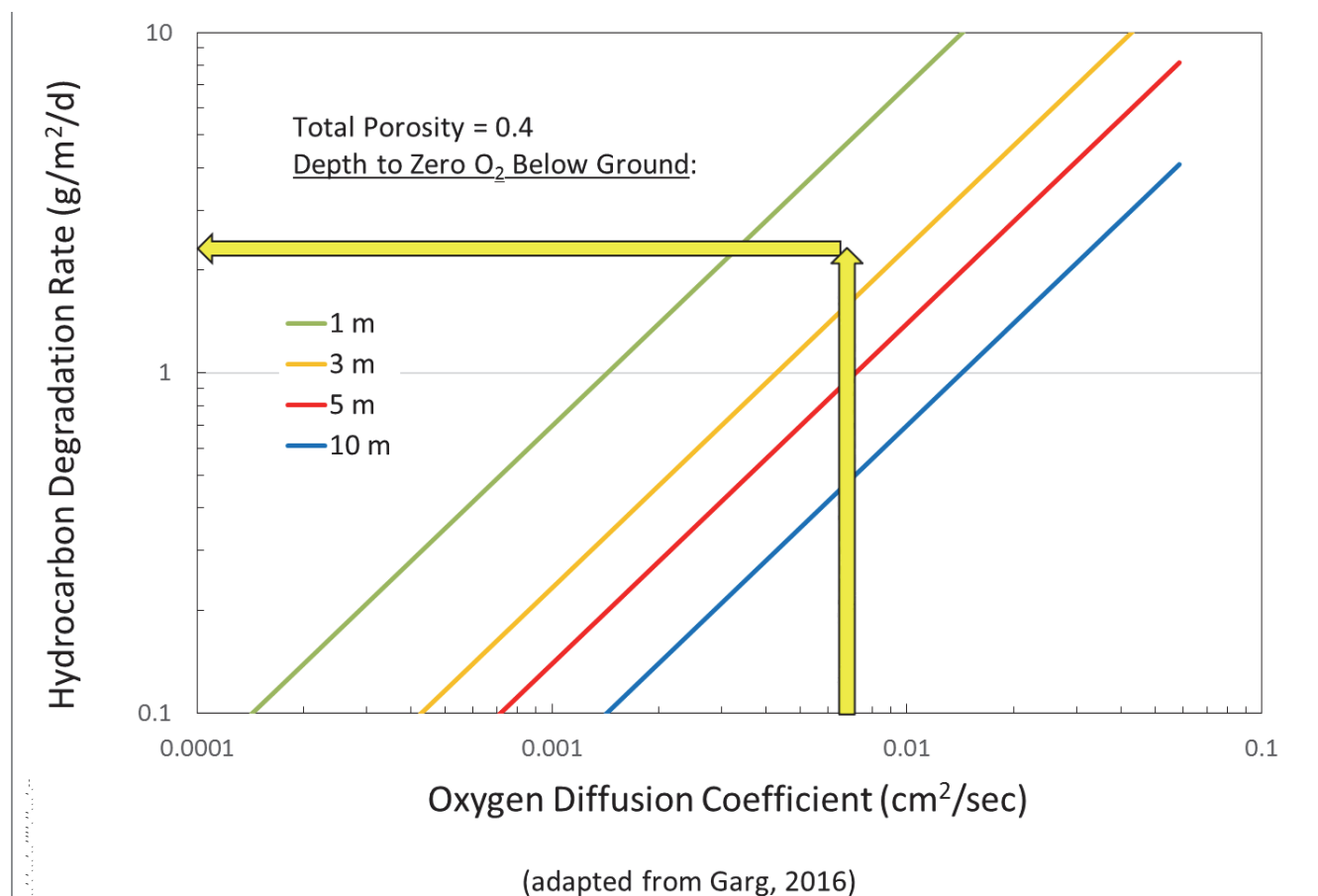


Figure B-8—Estimated Hydrocarbon Degradation Rate Using Effective Oxygen Diffusion Coefficient and Depth

Of note is effective vapor diffusion coefficients were previously estimated (not shown on Table B-4) two years earlier than the NSZD study reported herein. The results differed, but the differences were not uniform across locations or depth. For example, at NSZD-1 and NSZD-4, the effective diffusion coefficients are higher than previously estimated, with a maximum of two times difference observed at NSZD-4. In contrast, diffusion coefficients were lower than previously estimated at NSZD-2 and NSZD-3, with a diffusion coefficient at NSZD-2 that was 0.4 times lower than previously estimated.

Variability is expected in effective vapor diffusion coefficients due to climatological and other factors including moisture content and temperature. While seasonal changes may affect estimated soil gas diffusion coefficients, these changes may also affect other subsurface conditions—such as water table elevation, the relative portions of LNAPL exposed to volatilization or dissolution processes, and the vertical position of the hydrocarbon oxidation zone. Because there is a direct relationship between the soil vapor diffusion coefficient and the calculated NSZD rate, in situ vapor diffusion coefficient testing should be performed each time the gradient method is applied at a site.

B.3.1.3 Estimation of NSZD Rates

The approach chosen to estimate NSZD rates at this site was based on calculating the flux of O_2 consumption in the subsurface. As discussed in 4.1 and 7.2, there are other gradient method calculation bases such as CO_2 and CH_4 . The decision to use O_2 was a site-specific judgment based on review of the site-specific soil gas profiles. The approach assumes that anaerobic degradation products (such as CH_4) are completely oxidized upon reaching the top of the hydrocarbon oxidation zone, making O_2 consumption solely stoichiometrically indicative of total LNAPL mass losses. This condition held true for all locations except NSZD-1, where an NSZD estimate was not made.

As discussed above, and excluding NSZD-1 for the aforementioned reasons, hydrocarbon oxidation is generally occurring within the 3 to 7 ft bgs depth interval in the upper portion of the vadose zone at locations NSZD-2 through NSZD-4. Based on this observation, the lower boundary control point for the gradient method calculations (see 4.2.2 for details) was positioned at the second soil gas probe depth (ranging between 6.5 and 7 ft bgs). This probe depth was selected because it was within the hydrocarbon oxidation zone and thought most representative of NSZD processes. Selection of a shallower depth, where natural soil respiration processes were thought to dominate, would impart an undesirable bias on the results.

The differences between O_2 in atmospheric gas and measured O_2 concentrations at the second soil gas probe depth were used to determine the O_2 gradient and, thus, were used as a basis for estimating the NSZD rate.

The effective O_2 diffusion coefficients estimated from the shallowest sampling probes were used to estimate flux because these probes were generally positioned in the middle of the upper and lower boundary control points and are more representative of the diffusion that is occurring.

LNAPL loss rates were calculated based on an assumed LNAPL density of 0.82 g/mL and a representative hydrocarbon composition of $C_{10}H_{22}$ (decane).

For example, at NSZD-3, the depth to the base of the hydrocarbon oxidation zone is conservatively estimated to be 7 feet (2.13 m) (i.e. the nearest measured depth below the apparent zone). At this location, O_2 was measured at 0.5 % (0.007 kg/m³). The concentration of O_2 at the land surface (0' depth) is assumed to be atmospheric at 20.95 % (0.295 kg/m³). Using Equation 4.5, the O_2 gradient is:

$$\frac{dC}{dz} = \frac{c_2 - c_1}{z_2 - z_1} = \frac{0.295 - 0.007}{2.13 - 0} = 0.135 \frac{\left(\frac{kg O_2}{m^3}\right)}{m}$$

The resulting O_2 flux (J_{O_2}) is the product of the O_2 gradient and the effective O_2 diffusion coefficient. Using Equation 4.6 and converting units, gives:

$$J_{O_2} = D_v^{eff} \frac{dC}{dz} = 0.006 \frac{cm^2}{s} \times \frac{0.135 \frac{kg O_2}{m^3}}{m} \times 86400 \frac{s}{d} \times 0.0001 \frac{m^2}{cm^2} \times 1000 \frac{g}{kg} = 7.0 \frac{g O_2}{m^2 d}$$

Converting from O_2 mass flux to a volumetric hydrocarbon NSZD rate,

$$J_{NSZD-vol} = \frac{7.0 \frac{g O_2}{m^2 d} \times 0.25 \frac{g HC}{g O_2}}{0.82 \frac{g HC}{cm^3} \times 10.76 \frac{ft^2}{m^2} \times 1000 \frac{cm^3}{L} \times 3.7854 \frac{L}{gal}} = 5.3 \times 10^{-5} \frac{gal HC}{ft^2 d}$$

Only one round of NSZD measurements was made in this case study; therefore, as specified in 3.3.4, it is inappropriate to scale them up to an annual rate without an assessment of seasonal changes in subsurface conditions that may affect the NSZD rates. However, for ease of hypothetical conceptualization of NSZD and comparison to volumetric removal rates from other remediation technologies, they are reported herein in the units of hypothetical annual gallons per acre per year (gal/ac/yr). The estimated hypothetical annual NSZD rates using the gradient method ranged from approximately 580 to 1,200 gal/ac/yr (Table B-5).

Table B-5—Summary of Calculated NSZD Rates

Location	Equivalent LNAPL Loss Rates (g/m ² /d)		
	Gradient Method	Passive Trap Method	DCC Method
		Blank- and ¹⁴ C-corrected	Background-corrected
NSZD-1	NR	0.5	NM
NSZD-2	2.5	2.4	NR
NSZD-3	1.7	2.2	2.0
NSZD-4	1.2	0.33	0.34
Background	NM	0.27	0
Average within the LNAPL Footprint	1.8	1.3	1.2
NOTE g/m ² /d = grams per square meter per day (1 g/m ² /d = 480 gal/ac/yr) gal/ac/yr = gallons per acre per year DCC = dynamic closed chamber NM = not measured with this method at this location NR = not reported due to insufficient data or instrument malfunction Results are presented to two significant figures.			

It is important to note that this site-specific application of the gradient method did not include a background correction. As evidenced by the results of two other methods (see B.3.2 and B.3.3), the site appears to have a relatively high background flux of CO₂ and presumably O₂ consumption and some fossil fuel-related CO₂ was found at the Background monitoring location used for the passive flux trap and DCC methods. This suggests that the results from the gradient method likely overestimate the actual NSZD rates at this site. A background soil gas sampling probe cluster located in an area absent of hydrocarbon impacts in soil and NSZD-derived gases would have helped address this potential inaccuracy.

B.3.2 Passive Flux Trap Results

The laboratory results of CO₂ efflux measurements obtained from deployment of the passive flux traps are presented in Table B-6. Trip blank-corrected total CO₂ efflux values ranged from 0.72 μmol/m²/s at Background to 7.4 μmol/m²/s at NSZD-2. NSZD rates obtained from co-located duplicate traps were relatively consistent and near an industry-acceptable RPD of 30 %. After applying a background correction using ¹⁴C radiocarbon analysis (see procedures in 5.4.2), NSZD-derived CO₂ efflux values ranged from 0.20 μmol/m²/s at Background to 2.4 μmol/m²/s at NSZD-2.

An arithmetic mean of the duplicate trap results was used to estimate a representative CO₂ efflux and LNAPL loss rate for each location. Estimated equivalent hypothetical annual LNAPL loss rates ranged from 130 gal/ac/yr at Background to 1,100 gal/ac/yr at NSZD-2. The observation of fossil fuel-derived (¹⁴C-depleted) CO₂ efflux at the background location may indicate the presence of some degree of hydrocarbon occurrence (i.e., the location is not a true “background”), horizontal migration of CO₂ produced elsewhere over the LNAPL footprint, or the presence of non-petroleum ¹⁴C-depleted organic material within the subsurface.

Figure B-9 graphically represents the trip blank-corrected total CO₂ efflux and the ¹⁴C-corrected efflux measured by each trap. The ¹⁴C-corrected efflux represents the portion of CO₂ attributable to NSZD of petroleum hydrocarbons or fossil fuel-derived sources. The difference between the total efflux and the ¹⁴C-corrected efflux represents the estimated CO₂ flux from natural soil respiration. The results indicate that the greatest flux of “modern” (non-petroleum) CO₂ was observed at NSZD-2; this area is a grass-covered area within the terminal. The lowest modern CO₂ efflux was measured at NSZD-1, a gravel-covered area with negligible vegetation. In general, locations dominated by modern carbon efflux were in grassy vegetated areas, consistent with a greater degree of naturally-occurring respiration in shallow root zone soils. These results also indicate that natural soil respiration rates vary

Table B-6—Passive CO₂ Trap Method Results

Location		CO ₂ Flux Blank-corrected Total $\mu\text{mol}/\text{m}^2/\text{s}$	Relative Percent Difference	LNAPL Loss Rate Blank-corrected Total $\text{g}/\text{m}^2/\text{d}$	CO ₂ Flux ¹⁴ C-corrected $\mu\text{mol}/\text{m}^2/\text{s}$	LNAPL Loss Rate ¹⁴ C-corrected $\text{g}/\text{m}^2/\text{d}$
NSZD-1	Trap 1	0.78	32 %	1.0	0.37	0.5
	Trap 2	1.08		1.4	0.40	0.5
	Average	0.93		1.2	0.39	0.5
NSZD-2	Trap 1	7.64	18 %	10.1	2.38	3.1
	Trap 2	6.36		8.4	1.21	1.6
	Average	7.00		9.2	1.80	2.4
NSZD-3	Trap 1	2.14	27 %	2.8	1.42	1.9
	Trap 2	2.81		3.7	1.89	2.5
	Average	2.48		3.3	1.66	2.2
NSZD-4	Trap 1	2.38	32 %	3.2	0.22	0.3
	Trap 2	1.72		2.3	0.27	0.4
	Average	2.05		2.7	0.25	0.33
Background	Trap 1	0.72	82%	0.9	0.21	0.3
	Trap 2	1.73		2.4	0.20	0.3
	Average	1.23		1.6	0.21	0.27

NOTE Two traps were deployed concurrently at each location within the LNAPL footprint. One trap was deployed during each period at the Background location.

LNAPL loss rates are calculated based on an assumed LNAPL density of 0.82 mg/L and a representative composition of C₁₀H₂₂ (decane).

$\mu\text{mol}/\text{m}^2/\text{s}$ = micromoles per square meter per second
 $\text{g}/\text{m}^2/\text{d}$ = grams per square meter per day (1 $\text{g}/\text{m}^2/\text{d}$ = 480 $\text{gal}/\text{ac}/\text{yr}$)
 $\text{gal}/\text{ac}/\text{yr}$ = gallons per acre per year

significantly across the site, and a simple background correction approach of measuring CO₂ efflux at a single unimpacted location may be overly simplistic. At this site, the natural soil respiration efflux was as CO₂ (and in some places even larger) than the efflux attributable to petroleum degradation. If the non-petroleum CO₂ efflux was erroneously attributed to petroleum degradation, the LNAPL loss rates would be overestimated by more than two to three times.

B.3.3 DCC Method Results

The field results of CO₂ efflux measurements obtained from use of the DCC are summarized in Table B-7. An arithmetic mean of individual hourly flux measurements was used to estimate an average CO₂ efflux for each of the three locations where viable data were collected.

Average total CO₂ efflux values observed were 0.82 $\mu\text{mol}/\text{m}^2/\text{s}$ at the Background location, 1.1 $\mu\text{mol}/\text{m}^2/\text{s}$ at NSZD-4, and 2.3 $\mu\text{mol}/\text{m}^2/\text{s}$ at NSZD-3. An efflux result is not reported for the NSZD-2 location because of a malfunction of the DCC unit. As with the passive flux trap method, a measurable background efflux of CO₂ was observed. The background efflux was measured at a single location, then subtracted from all DCC results.

For example, at NSZD-3, the average total CO₂ flux was 2.3 $\mu\text{mol}/\text{m}^2/\text{s}$. Using Equation 3.2 to subtract the background flux results in $(2.3 - 0.82) = 1.5 \mu\text{mol}/\text{m}^2/\text{s}$. Using Equation 3.3 (see Section 3.3.2) to convert from CO₂

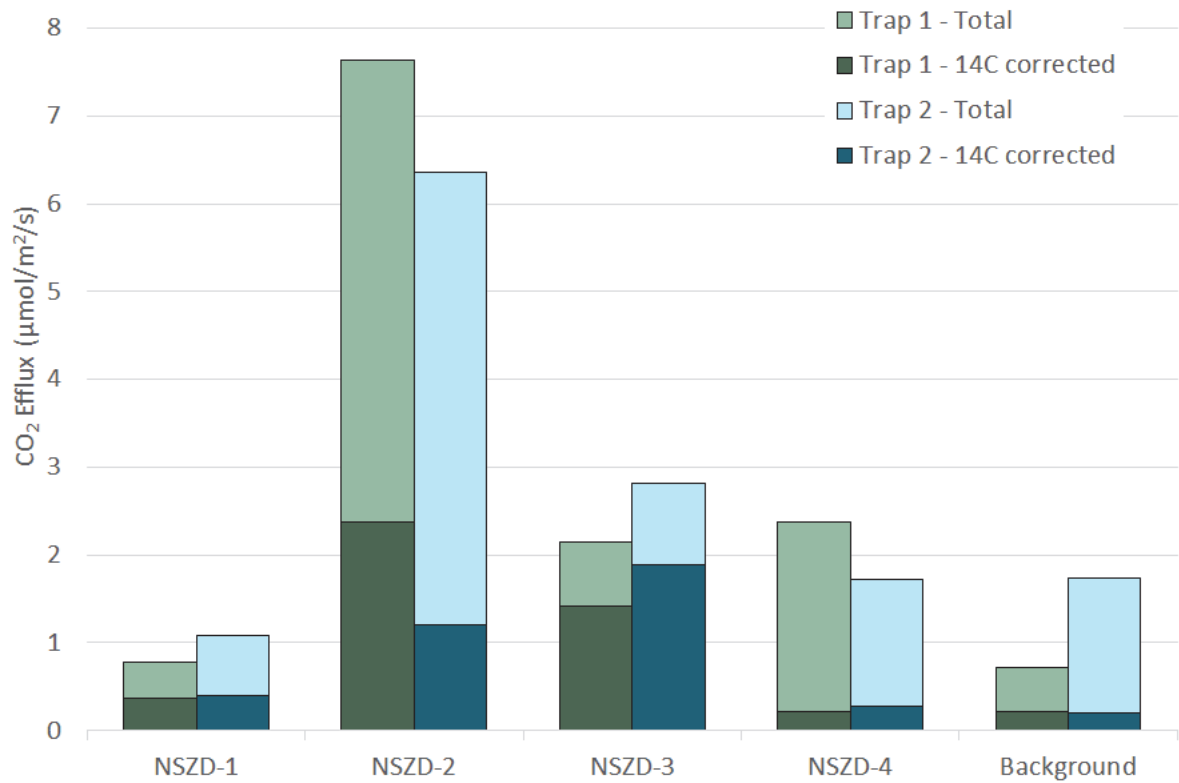


Figure B-9—Passive Flux Trap CO₂ Efflux Measurement Results

Table B-7—DCC Method Results

Location	Average CO ₂ Flux (μmol/m ² /s)	Equivalent LNAPL Loss (Uncorrected) (g/m ² /d)	Background-corrected NSZD Rate (g/m ² /d)
NSZD-2	NR	NR	NR
NSZD-3	2.3	2.8	1.8
NSZD-4	1.1	1.4	0.34
Background	0.82	1.0	0

NOTE

Arithmetic means of CO₂ flux measurements reported in time-series DCC data are shown.

μmol/m²/s = micromoles per square meter per second

g/m²/d = grams per square meter per day (1 g/m²/d = 480 gal/ac/yr)

gal/ac/yr = gallons per acre per year

NR = not reported due to instrument malfunction

mass flux to equivalent hydrocarbon volume, and following Lundegard and Johnson (2006) where the residual petroleum hydrocarbons are represented by the n-alkane decane, C₁₀H₂₂:

$$R_{NSZD-mass} = \left[\frac{J_{NSZD} \cdot m_r \cdot MW}{10^6} \right] \times \frac{86400 \text{ s}}{d}$$

(3.3)

Populating the variables, gives

$$R_{NSZD-mass} = \frac{1.5 \frac{\mu\text{molCO}_2}{\text{m}^2 \text{ s}} \times 0.10 \frac{\text{molHC}}{\text{molCO}_2} \times 142.3 \frac{\text{gHC}}{\text{molHC}}}{10^6 \frac{\mu\text{mol}}{\text{mol}}} \times \frac{86400 \text{ s}}{\text{d}} = 1.8 \frac{\text{gHC}}{\text{m}^2 \text{ d}}$$

Converting to volumetric units using Equation 3.6, gives

$$R_{NSZD-vol} = \frac{1.8 \frac{\text{gHC}}{\text{m}^2 \text{ d}} \times 264.17 \frac{\text{gal}}{\text{m}^3} \times 4046.86 \frac{\text{m}^2}{\text{ac}} \times 365 \frac{\text{d}}{\text{yr}}}{0.82 \frac{\text{gHC}}{\text{cm}^3} \times 10^6 \frac{\text{cm}^3}{\text{m}^3}} = 860 \frac{\text{galHC}}{\text{ac}'''\text{yr}}$$

The values at NSZD-4 and NSZD-3 correspond to background-corrected hypothetical annual NSZD rates of 160 and 860 gal/ac/yr, respectively.

Because of the large volume of data that were collected (hourly readings for approximately 16 days), the DCC method allows for detailed review of temporal changes in individual efflux measurements and investigation of potential correlations to soil moisture, ambient temperature, barometric pressure, and other environmental factors. Based on weather data collected during the study, and the soil moisture data collected via the auxiliary sensor on the DCC unit, soil moisture content appears to strongly influence CO₂ efflux. The top portion of Figure B-10 shows CO₂ efflux decreased sharply at the start of a 3 day, 0.9 in. rain event (0.02 in. on March 8, 0.86 in. on March 9, and 0.02 in. on March 10). There is a corresponding increase in soil moisture associated with the rain event, which apparently impeded the efflux of soil gas. Following the rain event, the soil moisture decreased and CO₂ efflux increased, with a “spike” in efflux observed, which was likely the result of soil gas flow paths being re-established and a short-term exhale of accumulated CO₂. The CO₂ efflux continued to increase as the shallow soil dried. The CO₂ efflux returned to within 1 μmol/m²/s of the pre-rain event levels in approximately 6 days, but due to the persistent elevated moisture, never returned to levels existing prior to the rainfall.

DCC data were also investigated for potential correlations to atmospheric temperature and barometric pressure. As shown on the bottom portion of Figure B-10, an excerpt of the data from the drier portion of the data record, a strong correlation between daily fluctuations in temperature and measured CO₂ efflux was observed; as temperature increased or decreased in diurnal cycles, CO₂ efflux varied by approximately 0.5 to 1 μmol/m²/s, with higher efflux occurring during periods of higher ambient temperature. This fluctuation is typical of CO₂ efflux associated with naturally occurring shallow root zone biological respiration (Xu et al., 2005). Barometric pressure fluctuations did not appear to strongly affect the CO₂ efflux.

The DCC method measures instantaneous CO₂ efflux across the ground surface. The instantaneous measured CO₂ fluxes varied from zero to a maximum rate of 3.1 μmol/m²/s at NSZD-3. This variability is likely due to the natural processes described above and would result in instantaneous hypothetical annual NSZD rates from zero to 1,800 gal/ac/yr. This short-term variability should be considered when interpreting NSZD rates generated by the DCC method. Section 6.2.6 has specific recommendations on how to manage uncertainty in DCC data collection.

B.3.4 Supplemental Data Results

The transducer data logger showed that the pressure gradients between barometric in atmosphere and deep soil gas in NSZD-3 generally ranged between 0.3 and 0.1 in. of water with a predominantly outward gradient (i.e. higher pressure at depth). At only five afternoon short-duration (1 to 5.5 hours) times during the approximately one-month equipment deployment (March to April) did the gradient temporarily reverse and indicate inward gradients (0 to 0.08 in. of water). This may be attributed to CH₄ generation within the hydrocarbon-impacted soils. As discussed above, the saturated zone is off-gassing CH₄ into the vadose zone and displacing N₂, as observed by the depleted N₂ concentration, and the relatively constant volumetric sum of CH₄ and N₂ at each soil gas monitoring depth. A more pronounced upward gradient was recorded at lower ambient temperatures, and during periods of higher soil moisture content, when shallow soil likely exhibits lower gas permeability.

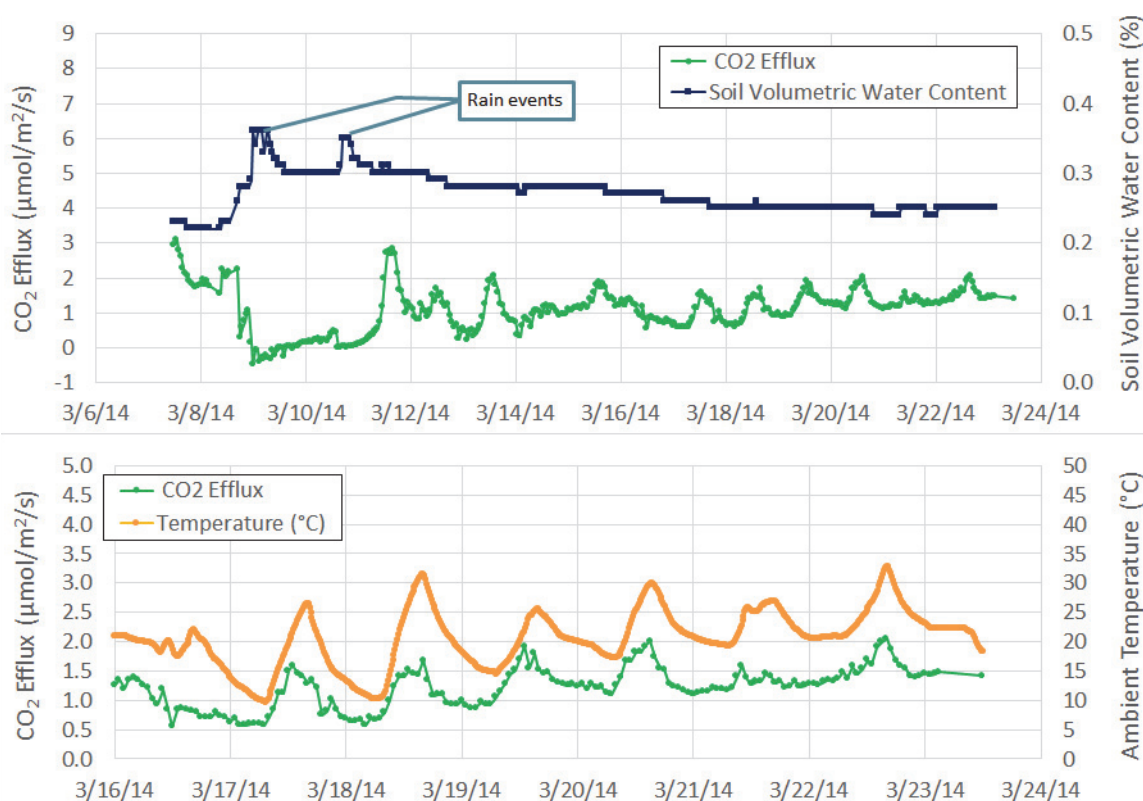


Figure B-10—DCC Results Compared with Soil Moisture and Ambient Temperature

B.3.5 Comparison of NSZD Rates

In general, the NSZD rates, summarized in Table B-5 and Figure B-11, generated from each monitoring method are of the same order of magnitude indicating that each method produced generally similar results. As discussed throughout this document, each method has its own inherent assumptions and potential biases. All things considered, the results of this comparison are positive. The NSZD rate calculations were evaluated to determine if adjustments of input assumptions would correct the variability between the methods; however, there was no single assumption that would account for the differences. Rather, the variability was likely due to site-specific and method-specific conditions as described below.

The DCC and CO₂ trap flux results both indicated measurable natural soil respiration at the background location. The background rates shown on Figure B-11 have been corrected for natural soil respiration by ¹⁴C measurements, and thus represent a “background” rate of petroleum hydrocarbon degradation.

The greatest difference in results between methods was observed at NSZD-4, where the gradient method indicated a rate of 1.2 g/m²/d (580 gal/ac/yr), and the passive flux trap method and DCC methods each indicated a rate of 0.34 g/m²/d (160 gal/ac/yr). Inspection of the soil gas profile presented in Figure B-6 and the CO₂ efflux in Figure B-9 suggest that while biological degradation of petroleum is occurring at NSZD 4, there is a measurable background efflux of CO₂ through the ground surface as measured by the CO₂ trap. This natural soil respiration would also have a depleting effect on subsurface O₂, which would impart a high bias on the gradient method results. This may at least partially explain the differences between method results at this location.

Please note that this was an NSZD study site and three NSZD monitoring methods were applied for the unique purpose of demonstration and comparison. Although the results from the three NSZD monitoring methods compared favorably considering the differences noted above, the differences in methods such as background correction methods, impacts due to rain events, and other site-specific conditions should be carefully considered when selecting

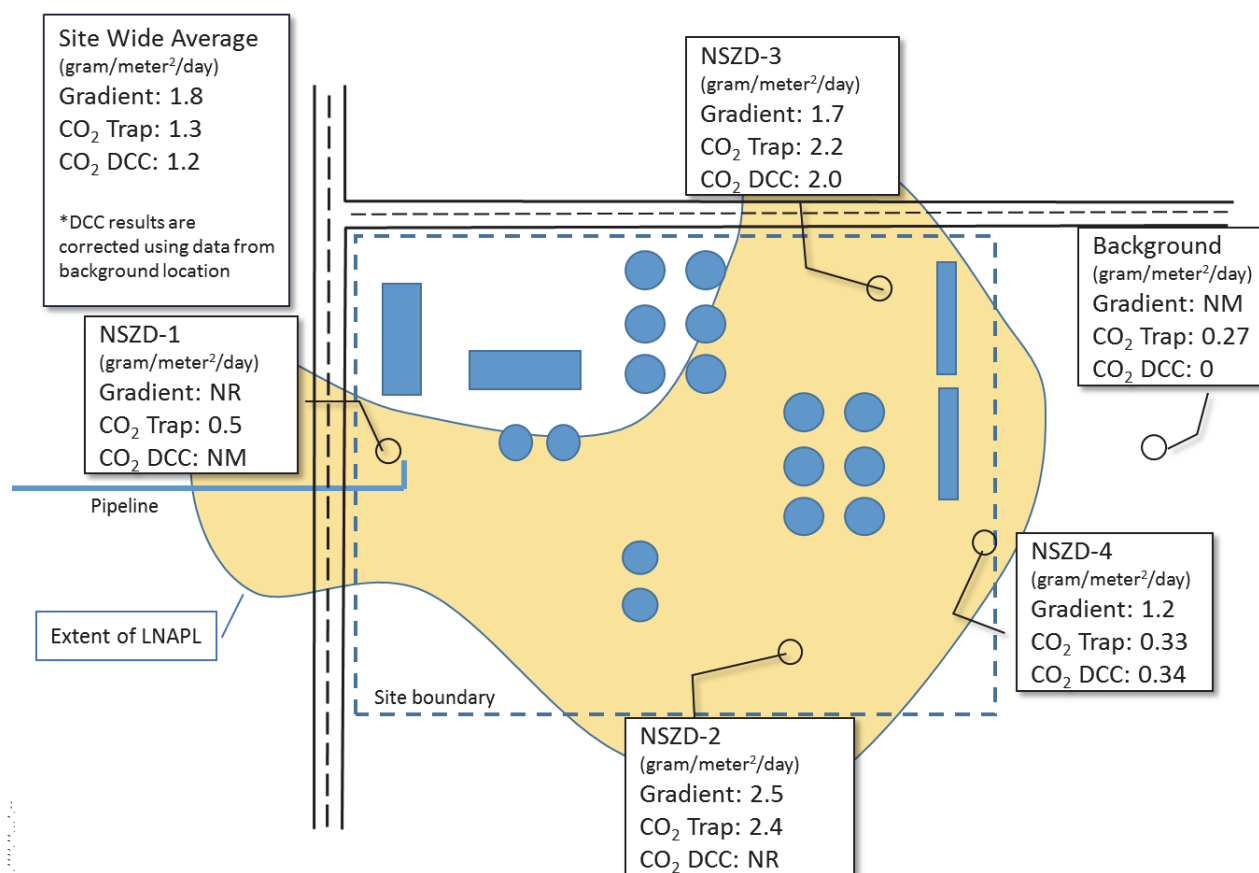


Figure B-11—Comparison of NSZD Rate Estimates

a method. Section 3.1.5 of this document addresses method selection based on site-specific data objectives and needs.

B.4 Conclusions

Three NSZD evaluation methods were applied at a petroleum products terminal site. Data collected during the study provided evidence that NSZD processes are occurring at the site. NSZD is contributing to long-term reductions in LNAPL mass at a rate on the order of 0.34 to 2.5 g/m²/d (160 to 1,200 gal/ac/yr), which spans the range predicted by the nomograms (2.0 to 2.5 g/m²/d).

Relevant findings regarding the NSZD measurements are summarized below.

- Despite their unique procedures and inherent assumptions, the NSZD rates calculated by each method are generally of the same order of magnitude. Albeit for somewhat of an academic purpose (i.e. this was a method demonstration study), all were capable of estimating NSZD rates at this site.
- The gradient method provides a detailed characterization of the soil gas profile and allows verification of important assumptions, such as elevated concentrations of CH₄ and CO₂ in the deep vadose zone and complete

CH₄ oxidation, to be verified. Its results can be used to quantify NSZD, but selection of a lower boundary control data point can be challenging due to location-specific soil and ground surface conditions.

- Results of the ¹⁴C isotopic analysis on the passive flux traps were invaluable for assessing background CO₂ efflux. They indicated that natural soil respiration varied at the site, and thus a simple subtraction of CO₂ efflux from a single background location may impart uncertainty on the results of the DCC method.
- Hourly CO₂ efflux data collected with the DCC method indicated that soil moisture content strongly influenced CO₂ efflux. Changes in CO₂ efflux following ambient temperature changes were also observed and are attributable to naturally occurring shallow biological activity in the root zone. This must also be accounted for in an NSZD monitoring program by performing NSZD monitoring during relatively dry and consistent temperature periods. Additionally, to more effectively characterize site conditions at the time of monitoring, effective soil vapor diffusion coefficient tests should be performed each time the gradient method is applied. Section 4.3.1 contains additional guidance on estimating the diffusion coefficient.

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