Quantification of Vapor Phase-related Natural Source Zone Depletion Processes

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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_7H_{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/ft2/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_2O	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	pounds per year
LCSM	LNAPL conceptual site model
LIF	laser 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 [CH_4]). 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 (CO_2) in the groundwater. They postulated that the transfer of atmospheric oxygen (O_2) 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 O_2, CO_2, CH_4, 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 CH_4 and smaller amounts of CO_2. Hydrocarbon compounds are volatilizing and offgassing along with the CH_4 and CO_2 from methanogenesis into the vadose zone. Where these gaseous NSZD byproducts meet atmospheric O_2, oxidation occurs. The oxidation of both CH_4 and