FACT SHEET

Natural Source Zone Depletion

MAY 2024

Introduction

Natural source zone depletion (NSZD) is a passive remediation approach that reduces light non-aqueous phase liquid (LNAPL) mass over time (Interstate Technology and Regulatory Council [ITRC] 2018). This fact sheet shares insights from several Department of the Navy (DON) installations where NSZD has been evaluated.

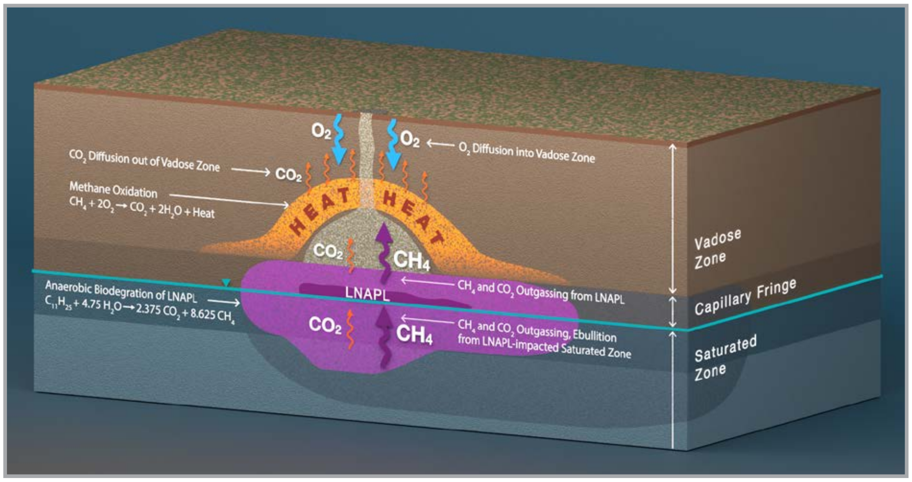

Figure 1. NSZD Process for LNAPL Mass Reduction (Courtesy of NAVFAC)

Background

Natural processes such as volatilization, dissolution, and biodegradation act in combination to reduce LNAPL mass over time. NSZD decreases both the saturation and mobility of the LNAPL in the subsurface. The biodegradation of LNAPL is a key component of NSZD (Figure 1). Under anaerobic conditions, methanogenesis degrades LNAPL and outgases methane (CH_4) and carbon dioxide (CO_2). As CH_4 gas rises through the vadose zone, the biodegradation process continues under aerobic conditions by oxidizing CH_4 to generate CO_2. This exothermic reaction requires sufficient oxygen (O_2) and produces heat in the vadose zone (ITRC 2018).

How Does It Work?

LNAPL can remain at a site even after decades of active remediation. At low-risk petroleum sites, NSZD can provide a passive approach to site management where active LNAPL recovery is no longer practical or cost-effective. A low-risk site suitable for NSZD has no LNAPL migration, a stable dissolved plume, and no vapor intrusion issues. NSZD rates can be measured in the field by monitoring CO_2 and/or heat generation in the subsurface (Table 1). The NSZD rate is calculated from the biodegradation stoichiometry of a selected hydrocarbon that is representative of the LNAPL at the site. The NSZD rate is expressed in gallons of LNAPL depleted per acre per year (gal/acre/yr). NSZD rate measurements typically range in the hundreds to thousands of gal/acre/yr. The site-specific rates can be measured as a snapshot in time (with CO_2 efflux or soil gas concentration gradient measurements) or monitored continuously over time (with temperature monitoring). For a comprehensive approach, the NSZD data collected from the vadose zone can be combined with additional supporting data. A monitored natural attenuation (MNA) evaluation can be conducted for petroleum constituents in the dissolved plume. In addition, LNAPL transmissivity measurements can help to evaluate free product recoverability and support decision-making to transition from active to passive remedial approaches (Naval Facilities Engineering Systems Command [NAVFAC] 2017).

How Can It Help?

An NSZD evaluation can help to accomplish the following:

- Provide quantitative data on site-specific LNAPL mass removal rates (gal/acre/yr)
- Estimate a cleanup timeframe given an understanding of the LNAPL volume present in the subsurface
- Serve as a basis of comparison of mass removal rates between active remediation (e.g., multi-phase extraction, air sparging/soil vapor extraction) and passive remediation and inform the use of treatment trains
- Support a transition from active to passive remediation when active LNAPL recovery is no longer practical or sustainable

NSZD Assessment Methods | **NAVFAC NSZD Case Studies** | **Lessons Learned**

NSZD Assessment Methods

NSZD can be assessed by collecting data using one or more of the methods summarized in Table 1.

Table 1. Summary of NSZD Assessment Methods

Measure CO_2 Efflux

Description	Data Collected	Equipment
Measure CO_2 levels near the surface. Convert the CO_2 efflux to NSZD rates.	CO_2 (including carbon-14 isotope analysis to distinguish fossil-fuel-related CO_2 from background as needed)	Passive CO_2 flux trap or dynamic closed chamber

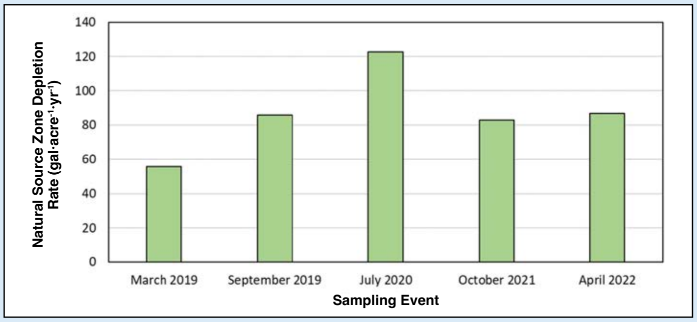

Figure 2. Site-wide Average NSZD Rates Based on CO_2 Flux Measurements at Yorktown Defense Fuel Supply Point (Courtesy of NAVFAC)

Note: The NSZD rates at this site ranged from approximately 60 to 120 gal/acre/yr. The results show an apparent seasonal variability in NSZD rates in the vadose zone, with the highest average CO_2 flux-based rate measured in the summer timeframe (July). The estimated average NSZD rate was 85 gal/acre/yr.

Measure Soil Gas Concentration Gradient

Description	Data Collected	Equipment
Measure soil gas profiles in the vadose zone. Convert the mass flux of target analytes to NSZD rates.	O_2, volatile hydrocarbons, CH_4, CO_2 (including carbon-14 isotope analysis to distinguish fossil-fuel-related CO_2 from background as needed), and estimated effective diffusion coefficient	Nested soil gas monitoring points

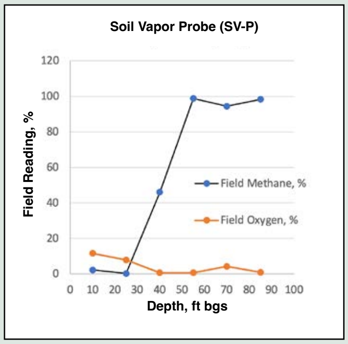

Figure 3. Soil Gas Concentrations with Depth at a Gasoline Station Site (Courtesy of Geosyntec)

Note: At a gas station site in Nevada, soil gas samples were collected in the field for laboratory analysis of CH_4, O_2, and CO_2 concentrations. Figure 3 shows example field readings from a soil vapor probe: high levels of methane were detected (at 98.8%) starting at 55 feet below ground surface (bgs), along with a corresponding decrease in O_2 levels down to 0.7%. The vertical diffusive flux of CO_2 was calculated based on the degradation of octane. The carbon-14 isotope analysis indicated that 80% of this flux was attributable to petroleum hydrocarbon degradation. The NSZD rate was estimated at 730 gal/acre/yr based on measurements across six soil vapor sampling points.

Measure Biogenic Heat Generation

Description	Data Collected	Equipment
Measure temperature profiles in the subsurface on a continuous basis. Monitor the increased temperatures compared to baseline. Calculate the heat flux and convert to NSZD rates.	Temperature. The subsurface temperature data can be compared between the LNAPL-impacted area and the baseline subsurface temperature in a clean, unimpacted area. Or mathematical models can be used to estimate the baseline temperature.	Temperature monitoring with thermocouples. Measurements can be made in the blank casing of existing monitoring wells.

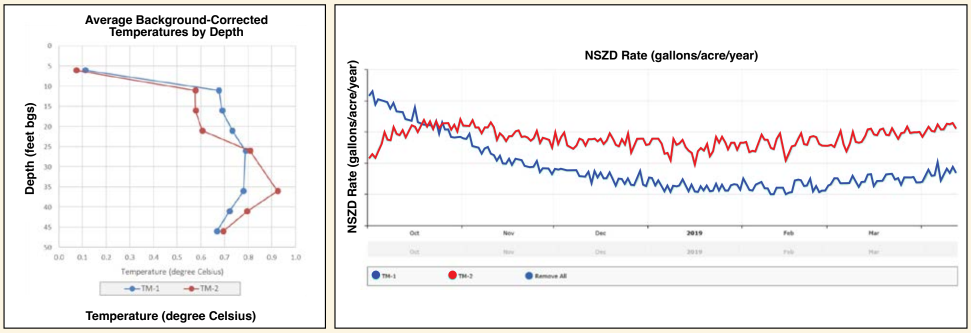

Figure 4. Temperature Profile with Depth (Left) and NSZD Rates (Right) based on Biogenic Heat Monitoring at Naval Air Weapons Station China Lake (Courtesy of NAVFAC)

Note: The NSZD rates at one location (TM-1) decreased from October to February when the measurements began to increase again.

Example results are provided from each of the three NSZD monitoring methods.

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NAVFAC NSZD Case Studies

NSZD has been evaluated at several DON sites to support remedy optimization and to transition to a more sustainable, passive remediation approach as feasible. Table 2 provides a summary of NSZD evaluations performed at five DON sites.

Table 2. DON Case Studies with NSZD Evaluations

Site / LNAPL Type	NSZD Evaluation Methods	Additional Supporting Data	Results
Yorktown Defense Fuel Supply Point / Weathered Navy Special Fuel Oil [1]	CO_2 flux measurements	LNAPL transmissivity measurements; LNAPL thickness monitoring, recovery, and mobility evaluation; groundwater quality monitoring, including geochemical data to assess biodegradation and plume stability	Estimated average NSZD rate was 85 gal/acre/yr. LNAPL body and dissolved plume remained stable. The Virginia Department of Environmental Quality approved shutdown of the active recovery system and a transition to NSZD monitoring with limited manual/passive recovery. After several years of NSZD monitoring, a Corrective Action Plan is currently under preparation to recommend site closure.
Naval Air Weapons Station China Lake Site 1 / Off-spec or used fuels, wash water containing degreasers and detergent [2]	CO_2 flux measurements and biogenic heat monitoring	LNAPL transmissivity measurements and mobility evaluation; laser-induced fluorescence (LIF) and ultraviolet optical screening tool (UVOST®) to evaluate LNAPL extent	Average NSZD rate was 47 gal/acre/yr by CO_2 flux measurements at 10 locations and 170 gal/acre/yr by thermal monitoring at 2 locations. The LNAPL plume was stable. The NSZD rate was estimated to be 40% of the LNAPL recovery rate. Manual or passive free product recovery at select wells continued.
Naval Air Weapons Station China Lake Site 44 / Off-spec or used fuels, wash water containing degreasers and detergent [2]	CO_2 flux measurements	LNAPL transmissivity measurements and mobility evaluation; LIF and UVOST® to evaluate LNAPL extent	Average NSZD rate was 170 gal/acre/yr. The dissolved plume and LNAPL footprint were shrinking. LNAPL recoverability was to be further evaluated.
Marine Corps Air Station Cherry Point Tank Farm B / JP-5 jet fuel, aviation gas [2]	CO_2 flux measurements	LNAPL transmissivity measurements and mobility evaluation; LNAPL composition analysis; groundwater and soil sampling and analyses, including geochemical data, to assess LNAPL biodegradation	Estimated average NSZD rate was 71.5 gal/acre/yr. LNAPL transmissivity tests indicated low recoverability. Groundwater sampling results indicated petroleum biodegradation products in the dissolved plume.
Naval Air Station Fallon Site 2 / Jet fuel, diesel, aviation gas [2]	CO_2 flux measurements	LNAPL transmissivity measurements and composition analysis; groundwater and soil sampling and analyses for volatile organic compounds, dissolved gases, and geochemical data to assess LNAPL biodegradation	Average NSZD rate was 170 gal/acre/yr, close to the free product recovery system operation of 160 gal/acre/yr. LNAPL transmissivity tests indicated low recoverability. Groundwater data indicated MNA occurrence.

Notes:
NAVFAC case study sources include [1] NAVFAC 2023 and [2] NAVFAC 2021.
All CO_2 flux measurements were performed with CO_2 traps for the Table 2 case studies.

NSZD evaluations have been conducted at several DON sites nationwide.

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Lessons Learned

Advantages, limitations, and cost considerations specific to the NSZD assessment methods are included in Table 3.

Table 3. Advantages, Limitations, and Cost Considerations of NSZD Assessment Methods

Method	Advantages	Limitations	Cost Considerations
CO_2 Efflux with Carbon Traps Method	• Widely accepted • Most common method deployed in the DON case studies	• Various site conditions (e.g., caliche layers, clay lenses, or other surface seals [asphalt, concrete, debris]) can impede transport of vapors to surface, resulting in an underestimate of NSZD rates. • Cutouts used to place traps over a paved surface may create a preferential pathway for CO_2 yielding an overestimate of NSZD rates. • High moisture conditions can interfere, blocking CO_2 migration. • Deep impacts (>25 ft bgs) may yield an underestimate of NSZD rates due to attenuation and dispersal of vapors in the subsurface.	• Number of carbon traps needed to adequately estimate NSZD rates at site
Soil Gas Concentration Method	• Conventional method familiar to most practitioners	• Method is not used as frequently due to relatively higher installation and labor costs. • Installation can be challenging under certain geological conditions (e.g., caliche layers). • Method is not effective in soils with tight formations (i.e., clays) due to limited feasibility of soil gas extraction.	• Relatively higher cost of multi-level soil vapor monitoring point installation and resulting labor
Biogenic Heat Monitoring Method	• Provides continuous data instead of just a snapshot in time • Recent advancements continue to improve the measurement of NSZD rates	• Potential equipment issues can occur (e.g., unit water tightness, data transmission challenges). • Type of well casing material can influence measurements (e.g., metal casings, solid vs. perforated casings). • Method is not as effective with shallow impacts (< 5 ft bgs) due to temperature interference from ambient air conditions.	• Can be costly at large sites that require multiple boring locations

For additional advantages and limitations related to NSZD implementation, please refer to the Federal Remediation Technologies Roundtable (FRTR) NSZD technology profile linked here. Overall lessons learned from the application of NSZD at DON sites are as follows:

- Considering multiple lines of evidence related to site risks, contaminant mobility, and NSZD rates can provide robust support for proposing a transition from active LNAPL recovery to a passive and sustainable approach.
- Collecting baseline information is crucial for assessing the effectiveness of NSZD. This includes temporarily pausing any remedial operations that impact site conditions and documenting water levels and free product thickness once the active remedial system has been shut down.
- Collecting multiple rounds of data in different seasons is important to account for seasonal variability in NSZD rates. Both seasonal fluctuations and precipitation-related variability of NSZD rates were observed and are more likely to occur at relatively shallow LNAPL sites.
- Demonstrating asymptotic removal of LNAPL and no LNAPL migration help to show that LNAPL has been removed to the extent technically feasible. LNAPL transmissivity tests may be conducted in conjunction with the NSZD evaluation process. The type of free product should also be considered with respect to transmissivity evaluations (e.g., gasoline versus a more viscous Navy Special Fuel Oil).

Disclaimer

Resources

ITRC. 2018. *LNAPL-3: LNAPL Site Management: LCSM Evolution, Decision Process, and Remedial Technologies. Note: See associated CLU-IN video at https://www.clu-in.org/conf/itrc/lnapl-3_020822/.*

NAVFAC. 2017. *New Developments in LNAPL Site Management.*

NAVFAC. 2021. *Case Study Review of Optimization Practices at Navy Petroleum Sites.*

NAVFAC. 2023. *Technical Memorandum for Natural Source Zone Depletion Monitoring of Light Non-Aqueous Phase Liquid at Yorktown Defense Fuel Supply Point Yorktown, Virginia.*