### *How can one estimate NSZD? Tier 3*

Natural Source Zone Depletion (NSZD) has emerged as an important new remediation alternative for LNAPL sites. Key references and a description of what they explain about NSZD are provided below:

- The ITRC's (2018) LNAPL Site Management—LCSM Evolution, Decision Process, and Remedial Technologies guidance is heavily influenced by the developments in measuring and applying NSZD for LNAPL site management, with over 100 specific mentions of NSZD in the document and a detailed NSZD appendix. More importantly, it provides detailed information on three frequently used NSZD assessment methods:
    - The gradient method, based on soil gas composition,
    - Carbon dioxide flux-based methods, including Carbon Traps and dynamic closed flux chambers (i.e., DCC-LI-COR), and
    - The biogenic heat monitoring method (Thermal Monitoring).

- Key vendors for these methods are:
    - EnviroFlux (Carbon Traps)
    - LI-COR (DCC- LI-COR)
    - Thermal NSZD (Thermal Monitoring)

- Garg et al.'s (2017) Overview of Natural Source Zone Depletion: Processes, Controlling Factors, and Composition Change provides a detailed review of how NSZD developed, key NSZD processes, potentially NSZD-controlling factors, and how NSZD affects the composition of LNAPL (see graphic to right). It is based on roughly 100 technical references.

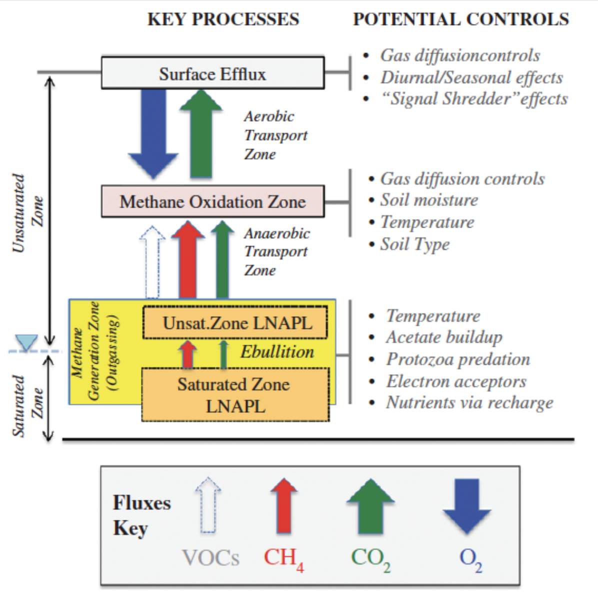


**Figure 2. Conceptual model of NSZD processes, gas fluxes, and controls in an LNAPL source zone. Adapted from multiple references shown in Table 1 and Figures 1 and 3. For simplicity, the LNAPL smear zone and the capillary fringe are not explicitly shown in the processes depicted in the conceptual model.**

- Kulkarni et al.'s (2020) Application of Four Measurement Techniques to Understand Natural Source Zone Depletion Processes at an LNAPL Site describes an extensive research project where four different NSZD measurement techniques were used at a site and then compared.

- Lari et al.'s (2019) Natural Source Zone Depletion of LNAPL: A Critical Review Supporting Modelling Approaches discusses key NSZD processes required to model NSZD and the capabilities of 36 models to accommodate 21 important phenomena.

- ESTCP's Environmental Wiki has an entry describing NSZD where the significance of NSZD is discussed along with NSZD stoichiometry, the gaseous expression of NSZD through gas evolution, and measuring temperature to determine NSZD (Palaia, T., J. Fitzgibbons, and P. Kulkarni, 2019).

- CRC CARE's (2018) Technical Report 44: Technical Measurement Guidance for LNAPL Natural Source Zone Depletion provides practical guidance on the measurement of NSZD rates using various available methods. The document applies to hydrocarbon sites that have a need for theoretical, qualitative, or quantitative understanding of NSZD processes. Its Appendix B contains a checklist for practitioners.

### Videos about NSZD

Two videos were developed for the NSZD article in the ESTCP Environmental Wiki. They can be viewed here:

- Carbon Traps NSZD
- Thermal Monitoring NSZD

### What NSZD Rates are Seen at Hydrocarbon Sites?

The following table from Garg et al. (2017) summarizes measured NSZD rates at various hydrocarbon sites in the U.S. The middle 50% of the NSZD rates range from 700 – 2,800 gallons per acre per year.

**Examples of Site-Wide Average NSZD Rate Measurements at Field Sites**

| NSZD Study | Number of Sites | Site-Wide NSZD Rate (All Sites) (Gallons/Acre/Year) | Site-Wide NSZD Rate (Middle 50%) (Gallons/Acre/Year) | Reference |
|---|---|---|---|---|
| Refinery terminal sites | 6 | 2100–7700 | 2400–3700 | McCoy 2012 |
| 1979 crude oil spill | 1 | 1600 | — | Sihota et al. 2011 |
| Seasonal range | | 310–1100 | — | Sihota et al. 2016 |
| Refinery/terminal sites | 2 | 1100–1700 | 1250–1550 | Workgroup, L.A. LNAPL 2015 |
| Fuel/diesel/gasoline | 5 | 300–3100 | 1050–2700 | Piontek et al. 2014 |
| Diverse petroleum sites | 11 | 300–5600 | 600–800 | Palaia 2016 |
| All studies | 25 | 300–7700 | 700–2800 | |
| Saturated zone electron acceptor biodegradation capacity | **9** | **0.4–53** | **1.7–19** | This paper (see Appendix S1) |

Notes: Middle 50% column shows the 25th and 75th percentile values. To demonstrate the significance of methanogenesis, NSZD rates calculated from the biodegradation capacity of electron acceptors in the saturated zone, ignoring methanogenesis, are shown in the last row.

Similarly, the table below summarizes a dataset of 31 distinct sites encompassing over 3,000 measurements from three different methods (DCC-LICOR, Carbon Traps, and Thermal Monitoring) was compiled. Measured average source area NSZD rates ranged from 655 to 152,470 liters per hectare per year, with a median of 8,750 liters per hectare per year (Rosansky et. al., 2021).

**Summary of NSZD Rates from 31 Sites**

| Fuel Type | Fuel Carbon Range | Number of Distinct Sites | Total No. of Measurements | Range of NSZD Rates Measured (L/ha/yr) | Median NSZD Rate (L/ha/yr) |
|---|---|---|---|---|---|
| Natural Gas Liquid* | C3-C6 | 5 | 1661 | 1,590 - 54,800 | 4,700 |
| Mixed | -- | 6 | 855 | 1,760 - 57,060 | 4,400 |
| Crude Oil | C8-C44 | 2 | 77 | 2,250 - 24,000 | 7,700 |
| Gasoline | C5-C12 | 4 | 144 | 2,800 - 41,500 | 9,800 |
| Diesel and Jet Fuel | C9-C24 | 12 | 134 | 650 - 99,400 | 12,250 |
| Fuel-Grade Ethanol | C2H6O | 2 | 183 | 123,200 - 152,500 | 138,000 |
| **Total** | | **31** | **3054** | **Median:** | **8,750** |

*May also contain smaller amounts of C7-C12 hydrocarbons

### What Enhanced NSZD Rates are Feasible?

Hydrocarbon degradation can be enhanced with increase in temperature (Sustained Thermally Enhanced LNAPL Attenuation [STELA]) (Zeman et al., 2014; Kulkarni et al., 2017). Specifically, the Arrhenius Law can be used to estimate the potential NSZD rate enhancement with any externally created temperature increase up to 45°C. The Arrhenius Law estimates for most biological systems, the temperature coefficient is 2.0 (i.e., rates will double with a 10°C increase in temperature) (Atlas and Bartha 1986; Riser-Roberts 1992).

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