

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 CO₂ traps and flux chambers, and
 - The biogenic heat monitoring method.
- 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.
- 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

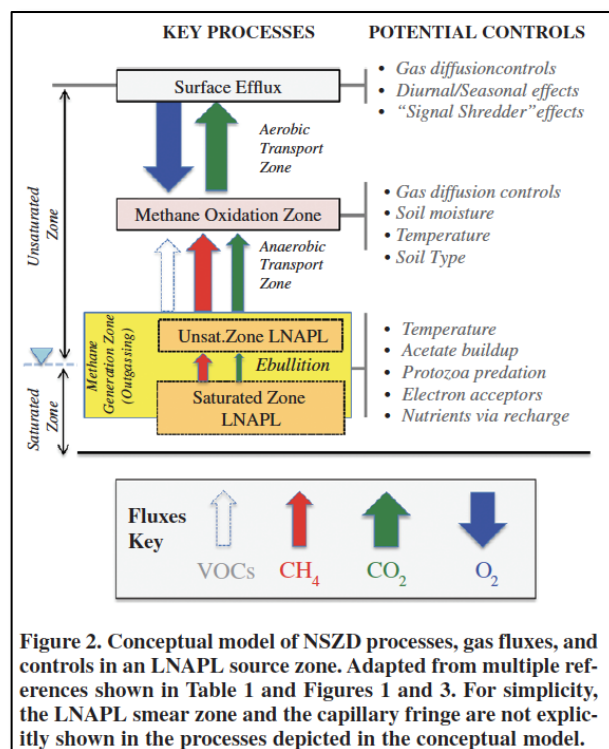


Figure 2. Conceptual model of NSZD processes, gas fluxes, and controls in an LNAPL source zone. Adapted from multiple references shown in Table 1 and Figures 1 and 3. For simplicity, the LNAPL smear zone and the capillary fringe are not explicitly shown in the processes depicted in the conceptual model.

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.

NSZD Study	Number of Sites	Site-Wide NSZD Rate (All Sites)	Site-Wide NSZD Rate (Middle 50%)	Reference
		(Gallons/Acre/Year)		
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.

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).

References

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- [Garg, S., Newell, C., Kulkarni, P., King, D., Adamson, D., Irianni Renno, M., Sale, T., 2017. Overview of Natural Source Zone Depletion: Processes, Controlling Factors, and Composition Change. Ground Water Monitoring and Remediation 37.](#)
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- [Kulkarni, P.R., King, D.C., McHugh, T.E., Adamson, D.T., Newell, C.J. 2017. Impact of Temperature on Groundwater Source Attenuation Rates at Hydrocarbon Sites. Groundwater Monitoring & Remediation, 37\(3\): 82-93. doi: 10.1111/gwmr.12226.](#)
- [Kulkarni, P.R., Newell, C.J., King, D.C., Molofsky, L.J. and Garg, S. 2020. Application of Four Measurement Techniques to Understand Natural Source Zone Depletion Processes at an LNAPL Site. Groundwater Monit R, 40: 75-88.](#)
- [Lari, S. Kaveh, Greg B Davis, John L Rayner, Trevor P Bastow, and Geoffrey J Puzon. 2019. Natural Source Zone Depletion of LNAPL: A Critical Review Supporting Modelling Approaches. Water Research 157: 630–46. Open Access.](#)
- [Palaia, T., J. Fitzgibbons, and P. Kulkarni. 2019. Natural Source Zone Depletion \(NSZD\). ESTCP Enviro Wiki. Accessed Feb. 2021.](#)
- Riser-Roberts, E. 1992. *Bioremediation of Petroleum Contaminated Sites* . Boca Raton, Florida : CRC Press Inc.
- [Zeman, N.R. , M.I. Renno , M.R. Olson , L.P. Wilson , T.C. Sale , and S.K. De Long. 2014. Temperature impacts on anaerobic biotransformation of LNAPL and concurrent shifts in microbial community structure . Biodegradation 25: 569– 585.](#)