

# Natural Source Zone Depletion (NSZD)

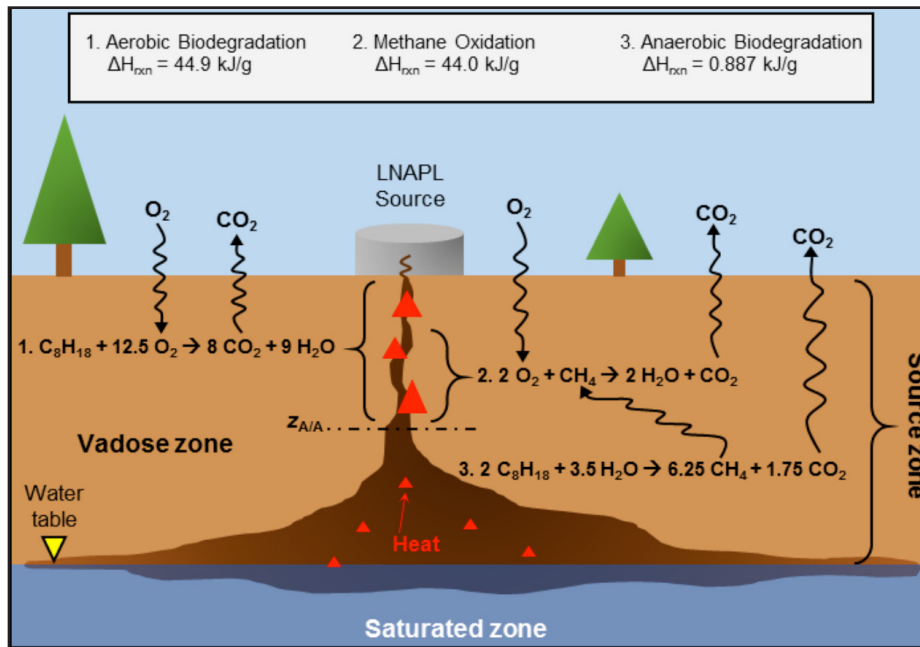
## A Key Part of the LNAPL Conceptual Site Model

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Following a Light Non-Aqueous-Phase Liquid (LNAPL) spill, characterization activities, including high-resolution site characterization (HRSC), are often used to determine the spatial extent of the contaminant, the location of the source, and the severity of the impacts on both soil and groundwater. After this initial characterization, the site owner must confront the crucial question: What's next? Most site owners and regulators will at this point turn their attention to remediation design, with the legitimate goal of restoring the site to its previously pristine condition.

While we environmental professionals are busy planning our responses to spills, natural soil processes are already underway. Soil microbial populations begin to adjust to the introduction of LNAPL compounds, resulting in the awakening of metabolic pathways capable of using the energy stored in LNAPL. These microbial mechanisms ultimately result in the biodegradation of petroleum, yet are often ignored or overlooked by site owners. However, biodegradation processes, collectively called Natural Source Zone Depletion (NSZD) have recently been recognized as crucial to the contaminated site's life cycle and are a key part of the formulation of the LNAPL conceptual site model (CSM).

NSZD includes microbially driven processes that result in the transformation of petroleum contaminants into dead-end inorganic products. This conversion, called *mineralization*, relies on the presence of microbes capable of degrading the contaminants, as well as the availability of electron acceptors like oxygen. Alternative electron acceptors (e.g., sulfate, nitrate, iron, manganese oxides) typically present in soil can be used by microbes for anaerobic pathways when oxygen



**Figure 1.** Schematic depiction of subsurface processes at an LNAPL spill

is not available until they, too, are depleted. Because oxygen is preferentially used by microbes as an electron acceptor and soil has a limited oxygen transport capacity, it is typically absent near the LNAPL source.

Although aerobic biodegradation is traditionally considered to be faster than anaerobic biodegradation, the relative importance of both processes at a site might be determined by the extent of contact between electron acceptors and the contaminant. Both aerobic and anaerobic pathways ultimately result in the production of carbon dioxide ( $\text{CO}_2$ ). This LNAPL-derived  $\text{CO}_2$  will rise through the soil column and eventually escape into the atmosphere.

In addition to those processes using “external” electron acceptors (i.e., those migrating toward the contaminant due to air or gas transport), many LNAPL-contaminated sources undergo methanogenesis, which results in the degradation of petroleum products into methane ( $\text{CH}_4$ ) and  $\text{CO}_2$ . This reaction, which does not require external electron acceptors, takes place below the aerobic/anaerobic interface within the soil column. As the upward-moving

$\text{CH}_4$  reaches this interface and contacts oxygen, it is typically rapidly oxidized to  $\text{CO}_2$ . If the flux of biodegradable carbon sources (including  $\text{CH}_4$ ) exceeds the soil's oxygen transport capacity, incomplete  $\text{CH}_4$  oxidation might occur. This situation, which can result in explosion hazards and increased risk of vapor intrusion, has been observed at a large ethanol-containing biofuel spill (Sihota et al., 2013).

### Why Are These Processes Important?

Acknowledging the interactions between soil microbes and petroleum contaminants has strong implications. First, it helps us better understand local soil and groundwater geochemistry in the context of a contaminated site. Second, it helps us realize that these processes will result in the in-situ mass depletion of organic contaminants.

From a practical viewpoint, NSZD can be a useful tool at all stages of a contaminated site's life cycle. Using NSZD principles (i.e., increased  $\text{CO}_2$  emissions from contaminated soils) to identify a geochemical footprint in the vadose

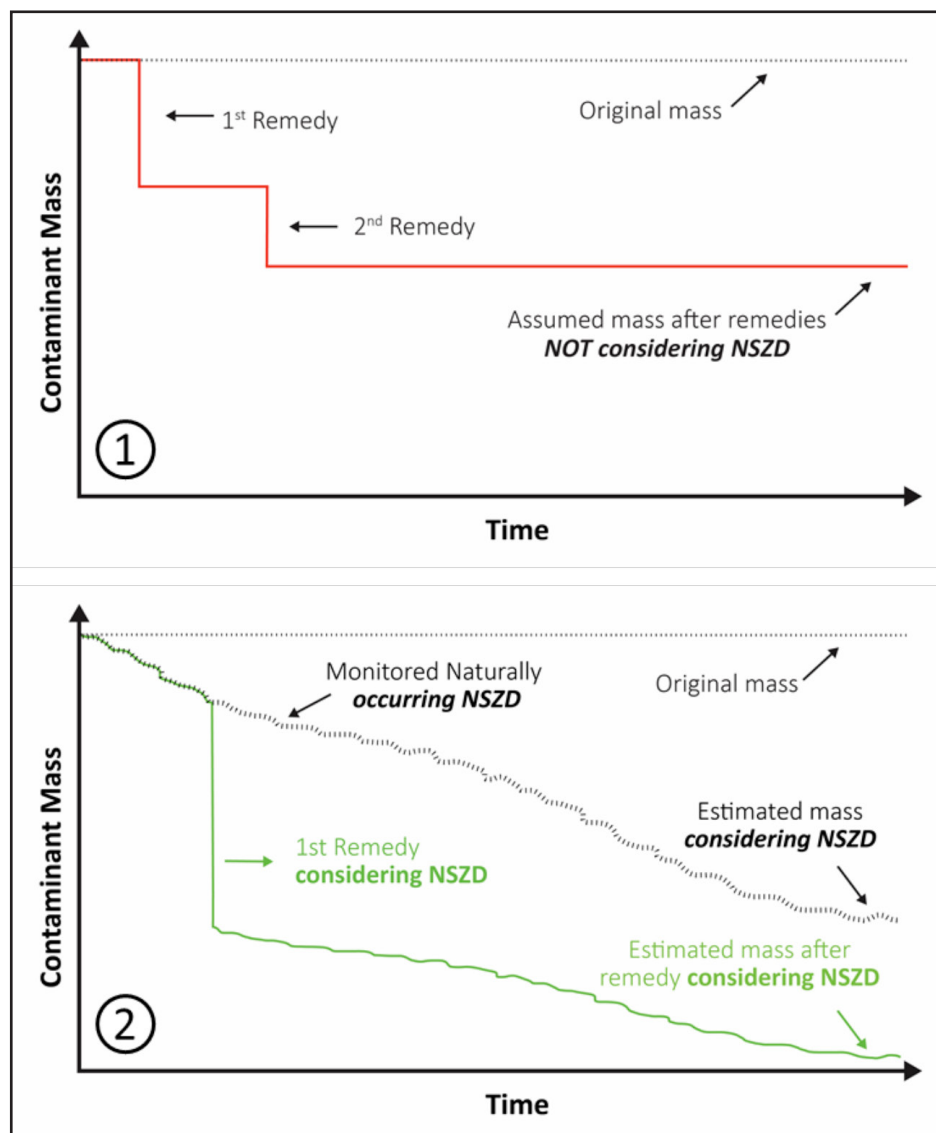
zone can help delineate the LNAPL source, which in turn helps site owners choose the locations of monitoring wells in order to better characterize the site and inform remedial decision making. At later stages, such as during remedy selection or transition, a quantitative measurement of the NSZD rate can provide a meaningful reference for the performance of the considered remedies. Additionally, NSZD reactions occur even when active remedies are in place. If we are willing to designate significant financial resources to site remediation, a sensible goal might be to increase the contaminant mass removal rate above the site's natural depletion rate.

### Measuring NSZD Rates

NSZD has been shown to occur at most petroleum-contaminated sites, and many techniques can be used to measure the rate at which these processes take place. The most common methods are based on the measurement of CO<sub>2</sub> efflux at or below the soil surface. The three CO<sub>2</sub>-based methods, namely the **concentration gradient method**, the **dynamic closed chamber method**, and **passive CO<sub>2</sub> flux traps**, deliver quantitative NSZD rates. Like all field sampling techniques, each of these methods has its own advantages and limitations.

The concentration gradient method was the first technique used to estimate NSZD rates and involves sampling soil CO<sub>2</sub> concentrations at different depths in the subsurface. The change in concentration at a particular plane in the soil column is proportional to the diffusive flux, according to Fick's law of diffusion. However, this method requires vertically distributed soil gas probes to be installed at the site, and the quality of results relies on an accurate determination of the soil's effective diffusion coefficient.

While the concentration gradient method is used to measure soil gas fluxes at specific soil depths, the other two methods, namely the dynamic closed chamber (DCC) and passive CO<sub>2</sub> flux traps, measure fluxes at ground level. The DCC is a vented chamber installed at the soil surface that is used to measure soil gas concentration changes. Several concentration measurements are



**Figure 2.** A conceptual depiction of mass losses over time at a hypothetical contaminated site: 1) accounting for only active mass removal remedies, and 2) also considering mass losses due to NSZD.

taken as the chamber fills with soil gas, and the CO<sub>2</sub> flux is calculated from the slope of the concentration-time regression. The DCC is most often used to measure soil gas fluxes during short deployments (typically a few minutes). However, long-term fluxes can be estimated with the DCC if enough repeated measurements are taken over an extended period to account for short-term CO<sub>2</sub> flux variability.

Passive CO<sub>2</sub> flux traps are deployed at the ground surface, where they capture CO<sub>2</sub> over an extended time period (e.g., 2 weeks) using a sorbent. After field deployment, the sorbent from each trap is analyzed for its CO<sub>2</sub> and <sup>14</sup>C concentrations. This isotopic correction allows the method to account for

only fossil-fuel-derived carbon during the quantification of NSZD rates. Passive CO<sub>2</sub> flux trap measurements provide long-term time-integrated average fluxes and are robust to daily barometric fluctuations.

All three of these methods rely on free-gas-transport pathways, meaning there can be no impermeable barriers to gas flow in the subsurface. NSZD rates measured at field sites using these three methods range from a few hundred gallons per acre-year to a few thousand gallons per acre-year.

A fourth measurement method, which makes use of soil temperatures and thermal gradients, is currently in development and is not considered quantitative. All pres-

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ently available NSZD monitoring methods are described in detail in a recent American Petroleum Industry (API) guidance document and in other technical literature (see “Timeline of Important NSZD Developments” and Additional Resources).

### The Importance of NSZD

If properly assessed, NSZD rates can provide an operational baseline for active remedies. No matter how advanced the remediation system, there comes a time when it is impossible or economically inefficient to remove any more contaminant from the ground because of low soil concentrations. NSZD can be particularly helpful in this situation—if NSZD rates are comparable to the performance of a remediation system, it might be possible to take advantage of this natural contaminant depletion rate. Evidence from the field, as well as the considerable body of literature backing up NSZD processes, should give us peace of mind in accepting that soil microbes will continue to remove contaminant left in the ground long after active remedies have stopped working.

Monitoring this natural depletion rate, therefore, keeps site owners up-to-date on the progress of contaminant removal efforts and informs regulators about the advisability of site closure.

### Frequently Asked Questions

**Q.** *How fast does petroleum biodegradation occur?*

**A.** A recent study found that NSZD-based loss rates measured at several field sites ranged from 700 to 2,800 gallons per acre-year (Garg et al., 2017). Although these rates are larger than expected, they are not high enough to achieve rapid site cleanup. For example, an apparently high NSZD rate of 1,000 gallons per acre-year only amounts to a free petroleum thickness decrease of about 1 mm. If an extraction or cleanup system is pushed to the point that it yields the same results as the natural microbial rate, this could be an indication that nature is achieving more than the active remedy. Sustained monitoring of NSZD rates is, therefore, crucial to the efficient and cost-effective management of active remedies.

**Q.** *What factors affect NSZD rates?*

**A.** Temperature has a very strong effect on the speed with which microbes break down petroleum products. As a result, NSZD rates at field sites are seasonally dependent, and rates are typically at a maximum in the fall. In general, 35°C to 40°C is the upper temperature tolerance limit for subsurface microbes, while microbial activity may be very slow or completely stopped at temperatures near or below freezing. Site-specific models can help us understand the relationship between temperature and microbial activity by assessing the depth distribution of local soil temperatures; an example of such a model is available for free at [BiogenicHeat.com](http://BiogenicHeat.com).

Another important factor impacting NSZD rates is the availability of electron acceptors. Some progress has been made by treating dilute dissolved plumes with external electron acceptors, such as sulfate (e.g., Kolhatkar and Schnobrich, 2017). In general, the success of these remedies is limited by the efficiency of contact between the contamination and the electron acceptors.

## Timeline of Important NSZD Developments

- 2006** Lundegard and Johnson measure spilled LNAPL mass losses using a mass balance applied to both the vadose (unsaturated) zone and to groundwater. Mass losses in the vadose zone were shown to be two orders of magnitude higher than those in groundwater.
- 2009** A new ITRC LNAPL Guidance Document describes mass balance methods for quantifying NA (Natural Attenuation) and NSZD rates in groundwater and in the vadose zone.
- 2011** A research group led by Dr. Uli Meyer at the University of British Columbia uses an agronomic technique to measure soil gas fluxes at grade, and correlates the changing concentrations with NSZD activity.
- 2014** A research team at Colorado State University develops a passive sampling technique which, when integrated with radiocarbon analysis, yields long-term CO<sub>2</sub> fluxes corrected for modern CO<sub>2</sub> contributions.
- 2017** The American Petroleum Institute publishes a Guidance Document and NAVFAC publishes “New Developments in LNAPL Site Management,” both describing different methodologies for the measurement of NSZD rates and the usefulness of those rates.
- 2018** An updated ITRC LNAPL Guidance Document highlights the importance of NSZD with respect to the LNAPL conceptual site model, and adds additional methods for measuring NSZD rates (incorporating those present in the 2017 API Guidance Document).

**Q.** How are LNAPL natural attenuation (NA), natural source zone depletion (NSZD), and monitored natural attenuation (MNA) related?

**A.** According to the ITRC LNAPL update document (ITRC, 2018), natural attenuation (NA) encompasses all natural processes that result in loss or neutralization of the contaminant without human intervention. NA includes both natural source zone depletion (NSZD) and monitored natural attenuation (MNA). NSZD specifically refers to mass loss from the unsaturated source zone caused by both physical and chemical processes, including biodegradation reactions. MNA is used to assess the rate of contaminant removal through the aqueous phase (see USEPA's OSWER Directive No. 9200-4.17). Because methanogenesis does not require external electron acceptors and its by-products (CO<sub>2</sub> and CH<sub>4</sub>) preferentially partition into the gas phase, field-measured NSZD rates often cannot be explained solely by the consumption of electron acceptors. Mass losses attributed to NSZD mechanisms are much larger than those related to MNA mechanisms (Lundegard and Johnson, 2006).

**Q.** Can NSZD rates be estimated based on the depletion of external electron acceptors?

**A.** Biodegradation reactions can be either aerobic (in the presence of oxygen) or anaerobic (in the absence of oxygen). Methanogenesis (an anaerobic process) is not reliant on external electron acceptors. This makes it impossible to estimate NSZD rates using only the degree of source zone electron acceptor depletion. However, aerobic and methanogenic NSZD pathways both ultimately produce CO<sub>2</sub>, meaning that in most cases NSZD rates can be accurately estimated using LNAPL-derived CO<sub>2</sub> fluxes.

**Q.** Can a site be completely cleaned up by NSZD processes in a few years?

**A.** NSZD is a long-term process. For a typical terrestrial petroleum spill, it might take decades for NSZD to remove significant contaminant mass. However, if active mass

removal methods have achieved some success, and the remaining contaminant mass poses a low risk to public and environmental health, performing NSZD calculations or studies may inform stakeholders about the usefulness of active and passive remedies in achieving site closure.

**Q.** Can NSZD monitoring be used at any LNAPL-contaminated site?

**A.** In general, yes, NSZD monitoring can be useful at most LNAPL-contaminated sites. NSZD rates can also be used to reinforce the conceptual site model in combination with other sources of data at all stages of the site's life cycle. For example, LNAPL-derived CO<sub>2</sub> fluxes can be used to delineate the extent of the contaminant during early site characterization, or NSZD rates can be used to assess the performance of various active remedies. Keep in mind that some site conditions, such as the presence of gas-impermeable/wet layers, interfere with the characterization of NSZD processes.

**Q.** Can NSZD be a final remedy for any LNAPL-contaminated site?

**A.** Yes, in the sense that we can sometimes take advantage of NSZD processes to let nature remove the last remnants of a contaminant in the subsurface following implementation of an active remedy.

**Q.** At how many LNAPL sites has NSZD been monitored to date?

**A.** NSZD rate measurements have been taken at hundreds of LNAPL sites and several DNAPL sites across North America. The widespread use of NSZD as a passive remedy and monitoring tool continues to grow every year, and NSZD is also quickly gaining acceptance in Europe and Australia.

**Q.** Does NSZD affect all LNAPL compounds equally?

**A.** This is likely not the case. It has been shown that microbes prefer certain compounds, such as those with lower molecular weights, over others. This means that the composition of the LNAPL contaminant is

likely enriched in less biodegradable compounds with time. It is therefore very important that we understand how these compositional changes affect the management of contaminated sites over the long term. ■

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#### Additional Resources

- American Petroleum Institute (2017) Quantification of Vapor Phase-related Natural Source Zone Depletion Processes, First Edition. <https://bit.ly/2E9C43>
- Garg S., Newell C.J., Kulkarni P.R., King D.C., Adamson D.T., Renno M.I., and Sale T. (2017) Overview of Natural Source Zone Depletion: Processes, Controlling Factors, and Compositional Change. *Groundwater Monitoring and Remediation* 37, 62-81.
- ITRC (2009) LNAPL Guidance Document. <https://bit.ly/2pRfSIk>
- ITRC (2018) Updated LNAPL Guidance Document. <https://lnapl-3.itrcweb.org/>
- Kolhatkar R. and Schnobrich M. (2017) Land Application of Sulfate Salts for Enhanced Natural Attenuation of Benzene in Groundwater: A Case Study. *Groundwater Monitoring & Remediation* 37, 43-57.
- Lundegard P.D. and Johnson P.C. (2006) Source zone natural attenuation at petroleum hydrocarbon spill sites—II: Application to a former oil field. *Groundwater Monitoring & Remediation* 26, 93-106.
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- Sihota N.J., Mayer K.U., Toso M.A., and Atwater J.F. (2013) Methane emissions and contaminant degradation rates at sites affected by accidental releases of denatured fuel-grade ethanol. *Journal of Contaminant Hydrology* 151, 1-15.
- Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites (OSWER Directive 9200-4.17). <https://bit.ly/2CKBe1o>
- Performance Monitoring of MNA Remedies for VOCs in Ground Water (EPA/600/R-04/027). <https://bit.ly/2C0mLg7>