

Applied NAPL Science Review

Demystifying NAPL Science for the Remediation Manager Volume 2, Issue 2, February 2012

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Applied NAPL Science Review (ANSR) is a scientific ejournal that provides insight into the science behind the characterization and remediation of Non-Aqueous Phase Liquids (NAPLs) using plain English. We welcome feedback, suggestions for future topics, questions, and recommended links to NAPL resources. All submittals should be sent to <u>the editor</u>.

LNAPL Natural Source Zone Depletion, Part 1: Occurrence and Confirmation

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Migrating LNAPL bodies can pose environmental risk via increased threat to down-gradient receptors, but stable LNAPL bodies can also pose environmental risk. Stable LNAPL bodies frequently serve as the source of toxic or obnoxious dissolved groundwater plumes that can impact drinking water resources and threaten ecological receptors. LNAPL bodies also can be the source of toxic or explosive subsurface vapors that can threaten structures and/or occupants.

Natural processes that occur in and around stable LNAPL source zones can mitigate their environmental risk over time by depleting the LNAPL source zone mass. Calculated loss rates can be significant, and NSZD can serve as a control or benchmark when comparing the effectiveness of remediation options. Natural source zone depletion (NSZD) processes include mass reduction by dissolution to groundwater and by mass volatilization to the vadose zone, followed by biodegradation of the dissolved phase in groundwater and the vapor phase in the vadose zone (Johnson et al., 2006).

Occurrence of NSZD Processes: NSZD processes tend to mitigate the risk of LNAPL source zones by reducing source zone mass over time. Different processes occur depending on whether the portion of the source zone being considered is submerged (in the saturated zone) or exposed (in the vadose zone).

<u>Submerged (Saturated) Source Zone:</u> NSZD processes occurring in the submerged source zone include dissolution of LNAPL constituents into groundwater and subsequent biodegradation in and around the submerged source. For multicomponent LNAPLs (e.g, gasoline, diesel and similar products), the lighter (and usually most toxic) compounds are more soluble in groundwater and are preferentially dissolved. Further mass reduction via biodegradation of dissolved LNAPL compounds can occur prior to groundwater exiting or leaving the source zone area. Over time, both the mass and the average toxicity of the submerged source zone LNAPL decrease due to the combination of dissolution and biodegradation. (See Part 2 of this series for determination of mass loss rates).

Mobile or Residual LNAPL



Figure 1: LNAPL mass depletion processes in submerged source zone (from ITRC, 2009).

<u>Exposed (Vadose) Source Zone:</u> NSZD processes primarily occurring in the exposed (vadose) source zone include the volatilization of LNAPL constituents into the vapor phase and subsequent biodegradation (Johnson et al., 1998). For multicomponent LNAPLs, the lighter (and usually most toxic) compounds are more volatile and preferentially enter the vapor phase. Biodegradation in the vadose zone soil column near the source zone may then degrade the vapor phase LNAPL compounds. Over time, the exposed source zone mass decreases in both toxicity and the ability to directly generate explosive vapors primarily due to the combination of volatilization and biodegradation (though secondary methane generation may continue for some time).



Figure 2: LNAPL mass depletion processes in exposed source zone (from ITRC, 2009).

Confirmation of NSZD Processes: Development of complete LNAPL conceptual site models (LCSM) includes an evaluation of the occurrence of NSZD processes associated with both the submerged and exposed portions of the source zone.

In the submerged (saturated zone) portion of the LNAPL source zone, mass dissolution to groundwater is indicated by higher concentrations of dissolved hydrocarbon at the downgradient edge of the LNAPL source zone compared to those at the upgradient edge. Evidence of submerged source zone mass reduction via biodegradation includes the downgradient depletion of electron acceptor (O_2 , NO_3 - and SO_4^{2-}) concentrations and downgradient enrichment of biodegradation by-product (Fe²⁺, Mn²⁺ and CH₄) concentrations (Johnson et al., 2006).

Indications that NSZD processes are occurring in the exposed (vadose zone) portion of the LNAPL source zone include:

- the presence of hydrocarbon soil gas with vertical concentration gradients (concentrations decrease at shallower depths above the source zone); and
- changes in TPH composition in soil gas compared to the source zone composition (i.e., higher proportion of volatile components in soil gas than in source zone).

Part 2 of this series will describe methods for estimating and applying an NSZD mass loss rate. The references listed below are a good starting point to learn more about NSZD processes.

References:

ITRC 2009 *Evaluating Natural Source Zone Depletion at Sites with LNAPL*, LNAPL-1, Technology Overview, Interstate Technology & Regulatory Council, Washington D.C., 76 pp. [Additional references in: <u>http://www.itrcweb.org/Documents/LNAPL-1.pdf</u>]

Johnson P.C., Bruce C., Johnson R.L. and Kemblowski M.W. 1998 In situ measurement of effective vapor-phase porous medium diffusion coefficients, *Environmental Science and Technology* **32**, pg 3405 – 3409.

Johnson P.C., Lundegard P. and Liu Z. 2006 Source zone natural attenuation at petroleum

hydrocarbon spill sites: I. Site-specific assessment approach, *Ground Water Monitoring and Remediation* **26**, pg 82 – 92.

Real World Limitations: A word of caution – natural source zone depletion (NSZD) is an important but complex process that includes many variables. While NSZD can be an effective, natural control on NAPL source zone mass, NSZD cannot be blindly relied upon as a control for LNAPL, dissolved phase, or vapor phase migration without detailed investigation and demonstration of its applicability at any given site. Identification of the occurrence of NSZD is an important part of a site's LNAPL Conceptual Site Model (LCSM) and <u>may</u> be an important component of a site remedy, subject to testing and verification.

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Context

Volume 2 (2011) of *Applied NAPL Science Review* (ANSR) is focused on tools and scientific concepts to improve NAPL conceptual site models (CSM). An accurate, detailed CSM will cost-effectively guide risk evaluations, remedial action decisions, technology selection, remedial design, and end point attainment (closure) evaluations.

Related Links

API LNAPL Resources

ASTM LCSM Guide

Env Canada Oil Properties DB

EPA NAPL Guidance

ITRC LNAPL Resources

ITRC LNAPL Training

ITRC DNAPL Documents

RTDF NAPL Training

RTDF NAPL Publications

USGS LNAPL Facts

ANSR Archives

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Coming Up

Look for more articles on LNAPL transmissivity as well as additional explanations of laser induced fluorescence, natural source zone depletion and LNAPL Distribution and Recovery Modeling in coming newsletters.

Announcements

ITRC 2-DAY CLASSROOM TRAINING:

Light Nonaqueous-Phase Liquids (LNAPL): Science, Management, and Technology April 5-6, 2012 Boston, MA

Register now at https://www.regonline.com/ITRC-LNAPL-MA

The Interstate Technology and Regulatory Council (ITRC) is offering a 2-day training class from the ITRC LNAPL team on April 5-6, 2012 in Boston, MA, in cooperation with ITRC state member, <u>Massachusetts Department of Environmental</u> <u>Protection</u>, and the <u>Northeast Waste Management Officials</u> <u>Association (NEWMOA)</u>.

Sponsor opportunities are available. Contact ITRC at training@itrcweb.org or 402-201-2419 to learn more.

In 2012-2014, ITRC may offer the LNAPL 2-day classroom training course in additional locations. Additional details will be provided at <u>www.itrcweb.org/crt.asp</u> when dates and locations are selected.

ASTM Guide for Calculating LNAPL Transmissivity is Now Available for Purchase at <u>www.astm.org</u>.

ASTM Standard E2856 - Standard guide for Estimation of LNAPL Transmissivity is now available

"LNAPL Transmissivity is a key metric for sites with LNAPL. The new ASTM Guide for Estimation of LNAPL Transmissivity is intended to help the industry generate more consistent calculations."

Andrew Kirkman, AECOM ASTM LNAPL Transmissivity Guidance Committee Chairman

ANSR readership has grown substantially since the first issue was published in January 2011. Thank you to everyone who has supported our mission to demystify NAPL science and share applied scientific NAPL tools and analyses to everyone around the globe. ANSR has readers in over 70 countries and every one of the United States of America. We welcome any feedback - please send comments to Mike Hawthorne.

ANSR now has a companion group on LinkedIn that is open to all and is intended to provide a forum for the exchange of questions and information about NAPL science. You are all invited to join by clicking <u>here</u> OR search for "ANSR - Applied NAPL Science Review" on LinkedIn.

If you have a question or want to share information on applied NAPL science, then the ANSR LinkedIn group is an excellent forum to reach out to others internationally.



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