

Open Environmental Restoration Resource (OER2) Webinar

Recent Developments in Petroleum Site Management

Presented by: NAVFAC Environmental Restoration Program

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- •Submit all questions via chat box throughout the presentation
- •Presentation is being recorded
- •Complete the webinar survey (main feedback mechanism)

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OER2 Webinar Series

•Why Attend?

- -Obtain and hear about the latest DOD and DON's policies/guidance, tools, technologies and practices to improve the ERP's efficiency
- -Promote innovation and share lessons learned
- -FEEDBACK to the ERP Leadership

•Who Should Attend?

- -ERP Community Members: RPMs, RTMs, Contractors, and other remediation practitioners who support and execute the ERP
- -Voluntary participation

Schedule and Registration:

- -Every other month, 4th Wed (can be rescheduled due to holidays)
- -Registration link for each topic (announced via ER T2 email)

•Topics and Presenters:

- -ERP community members to submit topics (non-marketing and DON ERPrelevant) to POCs (Gunarti Coghlan – gunarti.coghlan@navy.mil or Tara Meyers - tara.meyers@navy.mil)
- -Selected topic will be assigned Champion to work with presenter



Speaker Introduction



Chuck Newell (Presenter)

- Vice President of GSI Environmental Inc.
- Specializes in:
 - -Site characterization
 - -groundwater and surface water quality modeling
 - -risk assessments
 - -natural attenuation
 - -LNAPL/DNAPL problems
 - -Bioremediation
 - -Long Term Monitoring
- B.S. Chemical Engineering (Rice)
- M.S. Environmental Engineering (Rice)
- Ph.D. Environmental Engineering (Rice)

cjnewell@gsi-net.com

Michael Singletary (Presenter)

- Senior Engineer at NAVFAC SE
- Specializes in:
 - -groundwater hydrology
 - -fate and transport of contaminants
 - -bioremediation technologies
 - strategic planning and optimization of site investigation and remediation approaches.
- B.S. Civil Engineering (George Tech)
- M.S. Environmental Engineering (Georgia Tech)

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Recent Developments in Petroleum Site Management

Mike Singletary, NAVFAC Charles Newell, GSI Environmental

OER2 Webinar Series - October 2016



Wait, there's more....



- Status of Navy petroleum site cleanup efforts
- Key regulatory issues related to Navy petroleum sites
- Key tools for evaluating the practicability of LNAPL recovery
- New issues regarding Total Petroleum Hydrocarbons (TPH) and petroleum metabolites (fractionation)
- Measuring and applying Natural Source Zone Depletion (NSZD)
- Emerging methods to enhance NSZD

Status of Navy Petroleum Site Cleanup Efforts



- Navy Petroleum CTC \$183M
- Approximately 90% CTC in Phase 6 and 7
- Long-term costs for petroleum program likely underestimated
- Improved LNAPL conceptual site models needed to evaluate risk exposure and remedial options
- Optimization efforts needed to accelerate RC through riskbased closure options



Navy Petroleum CTC Breakout by Phase (\$K)

Two Ends of the Spectrum

<u>Typical</u> UST Cleanup • *Excavate contaminated soils* • *Extract free product for a while* • *MNA for plume*





<u>Difficult</u> UST Cleanup *In-situ treatment of source Complicated groundwater remedy Pump and treat*











Webinar Outline



- Key regulatory issues related to Navy petroleum sites
 - -Discharge to Surface Water
 - -Vapor Intrusion
 - **–LNAPL Recovery Limits**
- Key tools for evaluating the practicability of LNAPL recovery
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Discharge to Surface Water

•Discharge to Surface Water is Important Case:

- -<u>Alternate Concentration Limits (ACLs)</u>
 - If groundwater discharges to surface water
 - + no increase of constituents in surface water
 - + no human exposure = **Possible ACL**
 - Calculation based on GW models + mixing zones

-Transition zone (i.e., GW/SW interface)

- •Key element in site characterization
- Need <u>cross-media data</u> (GW, SW, sediment) to verify model results
- •Useful Navy technologies: Trident Probe, UltraSeep.

-Mixing zone rules

- State-specific from NPDES programs
- •Two criteria: Acute, lethal criteria "within short distance" & Chronic criteria at edge of mixing zone







Figure 3-6. Vertical screening distances for dissolved-phase source.

Figure 3-5. Vertical screening distances for LNAPL source.

LNAPL Recovery Limits

Old Conceptual Model

State	Measurable Level that Permits Closure	Closed Sites with LNAPL Greater Tha Measurable Level If So, Additional Criteria Used?	an ?		urce						
CA	Removed to extent practicable	Yes. "LUST sites can b closed if the required level of water quality wi be attained within a reasonable period of time. California has closed several sites with LNAPL."	2010; will NEIWPC(2006; Lur et al., 201		/PCC, ; Lund						
FL	0.01 ft	Yes. "A site with residu. soil contamination or groundwater contamination above cleanup target levels ca		NEIW 2006	/PCC,	th nan sl? al	Source Menatti.	МО	Maximum extent practicable	can be recovered in a cost-effective and efficient manner." Yes, "Site-specific criteria."	NEIWPCC 2006
		only receive No Further Action if there are institutional controls (deed restrictions) on th property."			Sementication according	be will nith fual	Menatti, 2010; NEIWPCC, 2006; Lund et al., 2014 NEIWPCC, 2006	NC NV	< 0.01 ft	No. 'No receptors and removal is technically and economically infeasible.' Yes. 'If a risk-based analysis was performed showing no vulnerable receptors and a fale and transport analysis performed showing that there was little potential for migrafion."	NEIWPCC, 2006; Lund et al., 2014 NEIWPCC, 2006
		н	41		Cleanup larget levy anly receive No FL Action if there are institutional contro (deed restrictions) property." Yes. "Only it BTE2 PAHs are ND or w below action level	irther Is on the Cand yell	NEIWPCC, 2006	RI TX	Unrecoverable or impractical	Yes "Closure can be granted when recoverable NAPL is still present if there are no receptors and the plume is stable."	Lund et al., 2014 NEIWPCC, 2006
		ТА		<0.01 ft	no other receptors Yes. 'Following Nu recovery activities, may be closed if p does not return in monitoring well in of 0.02 ft for a peri one year."	" APL a site roduct a excess lod of	NEIWPCC, 2006	UT VA	1/8-inch <0.01 ft	Yes. 'RBCA-based approach considered on site-specific basis.' Yes. 'The data should support the claim that the technologies used and/or evaluated are no longer effective and that	Menatti, 2010 NEIWPCC 2006; Steers, J., 2012; Lun
		н. - Ж			Yes. Obtained clo Illinois with notable thicknesses. Sile- basis, essentially a the same lines as Massachusetts. Yes. "Non-Stable is not present under	NAPL specific slong NAPL ar	Payne, 2016 Marra, 2014			addilional recovery is not practicable. If >0.01 fl exists also have to show: a) Remaining LNAPL and dissolved-phase constituents are not a risk to human health or the environment, and b).	et al., 2014
					current sile conditi and for the foresee future, and all NAF Micro-Scale Mobili removed if and to extent feasible bas upon consideration CSM principles. (C)	lans nable ?L with ity is the ied n of)				NSZD of the LNAPL body and natural attenuation of the dissolved-phase plume are documented as occurring at the site and are expected to further mitigate risk from the release, and c). The	
		м	41		Yes. "Recovery of LNAPL with a transmissivity great than 0.5 ft ² /day an	ter	Lund et al., 2014	WA	<0.01 fl	areal extent of the free phase plume at the sile is shown to be stable or decreasing* No. * Ecology won't close	NEIWPCC



Tn=Transmissivity Tn=Kn*bn Well LINAPL Kn=LNAPL Conductivity

New Conceptual Model

CALCULATION TOOLS

The American Petroleum Institute (API) provides a useful tool for calculating LNAPL transmissivity from baildown test data (API, 2012).

The American Society for Testing and Materials (ASTM) has developed standardized guidance (E2856-13) for estimating LNAPL transmissivity at a site (ASTM, 2013). The ASTM method provides procedures for estimating transmissivity by performing baildown tests, skimmer pump tests, performing continuous recovery with a treatment system, and by performing tracer tests.

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Former Midwestern Refinery LCSM Development



- Smear zone delineation (X, Y, Z)
- Review of historic conventional data
 - Wells with LNAPL
 - Dissolved phase indicators
 - Soil sample and PID indicators from soil borings
- Approximately 200 acre footprint smear zone of varying thickness and impact

Smear Zone extent





How To Use LNAPL Transmissivity



Transmissivity as a Performance Metric:



Difficult to recovery LNAPL hydraulically if T < 0.1-0.8 ft²/day

Four Methods To Get T_{LNAPL}



Standard Guide for Estimation of LNAPL Transmissivity¹

This standard is issued under the fixed designation E2856; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript pepilon (e) indicates an editorial change since the last revision or reapproval.

- 1. Manual Skimming Methods
- 2. Long-Term Recovery Based Methods
- 3. Short-Term Baildown Tests
- 4. Tracer Based Method

Smear Zone Transmissivity (Property of Fluid, Aquifer Material, and LNAPL Formation Thickness)

- LNAPL baildown tests conducted in all wells with LNAPL
- Transmissivity was used to focus remedial efforts where LNAPL mass recovery had a high likelihood of success
- Area of transmissivity over 1 ft²/day is 20 acres (of 200 acre smear zone)



✗ INTERSTATE

COUNCI

User Guide for the API LNAPL Transmissivity Workbook: A Tool for Baildown Test Analysis

API Regulatory and Scientific Affairs Department

API Publication 46xx (pre-publication draft) SEPTEMBER 2012

NOTE: This is a 'pre-publication' version of the API LNAPL Transmissivity Workbook that is provided to allow early access to this report. Minor formatting changes may occur prior to its formal publication.







Google: API Baildown Test LNAPL

Method 4: Calculating LNAPL Transmissivity From Tracer Tests



Figure 4. A 15-cm ID well equipped with pipes for (C_0 and C_{100}) standards and a cap for access to LNAPL in the well C_{well} .

ground, Water Measurement of LNAPL Flow Using Single-Well Tracer Dilution Tests to Evaluate LNAPL Flux at Seven Field Sites In the Ker Start for Start for Sever Field Sites

CSU: LNAPL Can be Moving Inside LNAPL Zone Without Increasing the LNAPL Footprint!





Figure 9. Comparison of the effects of inflow rate and loss rates on the extent over time of an oblong LNAPL body. The contours are given in years. The contour time increments are 40 years for panels (a), (b), and (c), 20 years for panels (d), (e), and (f), and 10 years for panels (g), (h), and (i).

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What is TPH?



- •TPH measures the Total Petroleum Hydrocarbons without quantifying concentrations of individual petroleum constituents
- •Total TPH alone do not indicate risk to human health or the environment



TPH Fraction Method



•Conservative toxicity and fate and transport characteristics are applied to estimate health and environmental risk



TPH Considerations

- •TPH can report false positives and register natural organics and petroleum degradation products
- •Background sources of non-hydrocarbons should be considered by reviewing chromatograms
- •Silica Gel Cleanup was designed to remove these polar compounds



Polar Metabolites at Hydrocarbon Sites



- But silica gel cleanup may be removing hydrocarbon metabolites
- "Polars" comprised of organic acids, alcohols and ketones, with few phenols
- •At one crude oil site:
 - -Polars concentrations about 2-3 times TPH-D concentration
 - Polar plume still expanding
- •Two different perspectives in these two papers

Groundwater

Crude Oil Metabolites in Groundwater at Two Spill Sites

by Barbara A. Bekins¹, Isabelle M. Cozzarelli², Melinda L. Erickson³, Ross A. Steenson⁴, and Kevin A. Thorn⁵

Monitoring&Remediation

Nature and Estimated Human Toxicity of Polar Metabolite Mixtures in Groundwater Quantified as TPHd/DRO at Biodegrading Fuel Release Sites

by Dawn A. Zemo, Kirk T. O'Reilly, Rachel E. Mohler, Asheesh K. Tiwary, Renae I. Magaw, and Karen A. Synowiec

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Original Conceptual Model for Natural Source Zone Depletion: Groundwater Mass Flux



Key factors for groundwater biodegradation mass balance:

- Delta dissolved oxygen
- Delta dissolved nitrate
- Delta dissolved sulfate
- Delta dissolved ferrous iron
- Delta dissoved methane

NSZD: Groundwater Mass Flux vs. Vapor Phase Mass Flux

Dissolved Plume





olatilization

Figure 2-2. Vapor transport-related NSZD processes.

Mobile or Residual LNAPL

Groundwater Flow_

- Oxygen gradient from surface into vadose zone
- Methane generation
- Carbon dioxide at surface



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New NSZD Conceptual Model: Vapor Phase Mass Flux is Much More Important





Lundegard and Johnson, 2006; Suthersan 2015

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Methane and "Ebullition"







Three Conventional Ways to Measure NSZD







Lundegard and Johnson, 2006

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What NSZD Rates are Being Measured?



NSZD Study	Number of Sites	Site-Wide NSZD Rate (gallon per acre per year)	Reference
Refinery terminal sites	6	2,100 - 7,700	McCoy et al., 2012
1979 crude oil spill	1	1,600	Sihota et al., 2011
Refinery/terminal sites	2	1,100 - 1,700	LA LNAPL Wkgrp, 2015
Fuel/diesel/gasoline	5	300 - 3,100	Piontek, 2014
Diverse petroleum sites	11	300 - 5,600	Palaia, 2016

Key Point: Measured NSZD rates in 100s to 1000s of gallons of LNAPL biodegraded per acre per year.



Locations across U.S. where carbon traps have been used to measure NSZD rates (E-Flux, 2015)

NSZD Conceptual Model





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NSZD Conceptual Model





Kansas Site: Subsurface Temperatures





Source: Emily Stockwell, Tom Sale Colorado State University

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Field Installation: Thermal Monitoring System





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Field Installation: Thermal Monitoring System





Thermocouple on temperature monitoring "stick"

Installation of stick using direct push rig.

Solar power supply and weatherproof box with data logger and wireless communications system.

ThermalNSZD

HOME TECHNOLOGY DEMO IMPLEMENT CONTACT CUSTOMER LOGIN

Thermal NSZD: Continuous Remote Monitoring of Natural Source Zone Depletion (NSZD)

The Thermal NSZD technology (patent pending) measures the rate at which natural biodegradation destroys free-phase product (LNAPL) in the subsurface by measuring the heat released by the microbial reactions.



Advantages of Thermal NSZD



One-time field installation of remote monitoring system with minimal O&M, no site visits, no sampling and no lab.

Daily temperature readings from vertical profiles of thermocouples.

Secured, read only access to site data for regulators.

www.ThermalNSZD.com



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"The color is a symbol for calm, cleanliness, and purity, but it also serves to contrast the light of the city, which is predominantly amber or bright white"



Pilot Tests: Casper Wyoming





Low-Cost Heating Elements using Heat Tape

Key Point:

- Increase in subsurface temperatures
 achieved
- Performance data analysis in progress





STELA: Heating and Core Results



Preliminary Data

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STELA Heat Delivery Methods







Thermal Conductance Heating



Electrical Resistance Heating



Borehole Heat Exchangers

Soil Solarization: Why Plastic?













Subsurface Heating Over Time





Key Points: Soil Solarization Pilot Tests

- Soil solarization using plastic is a potentially promising subsurface heating method
- Likely applicable for to enhance NSZD at LNAPL sites
- On-going work by CSU/GSI Understanding gas transport / venting options



Tufflite IV "The Greenhouse Film of the Future"

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Wrap Up



•Please complete the feedback questionnaire at the end of this webinar. We are counting on your feedback to make this webinar series relevant!

• Check the T2 email for upcoming OER2 Webinar Announcements!

•Thank you for participating!