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LNAPL transmissivity and NSZD/enhanced NSZD at a petroleum pipeline release site:

→ Is it time to transition to a nature-based LNAPL management strategy?

Welcome

Agenda

1. LNAPL Concepts
2. LNAPL Transmissivity
3. Natural Source Zone Depletion
4. Application: Case Study

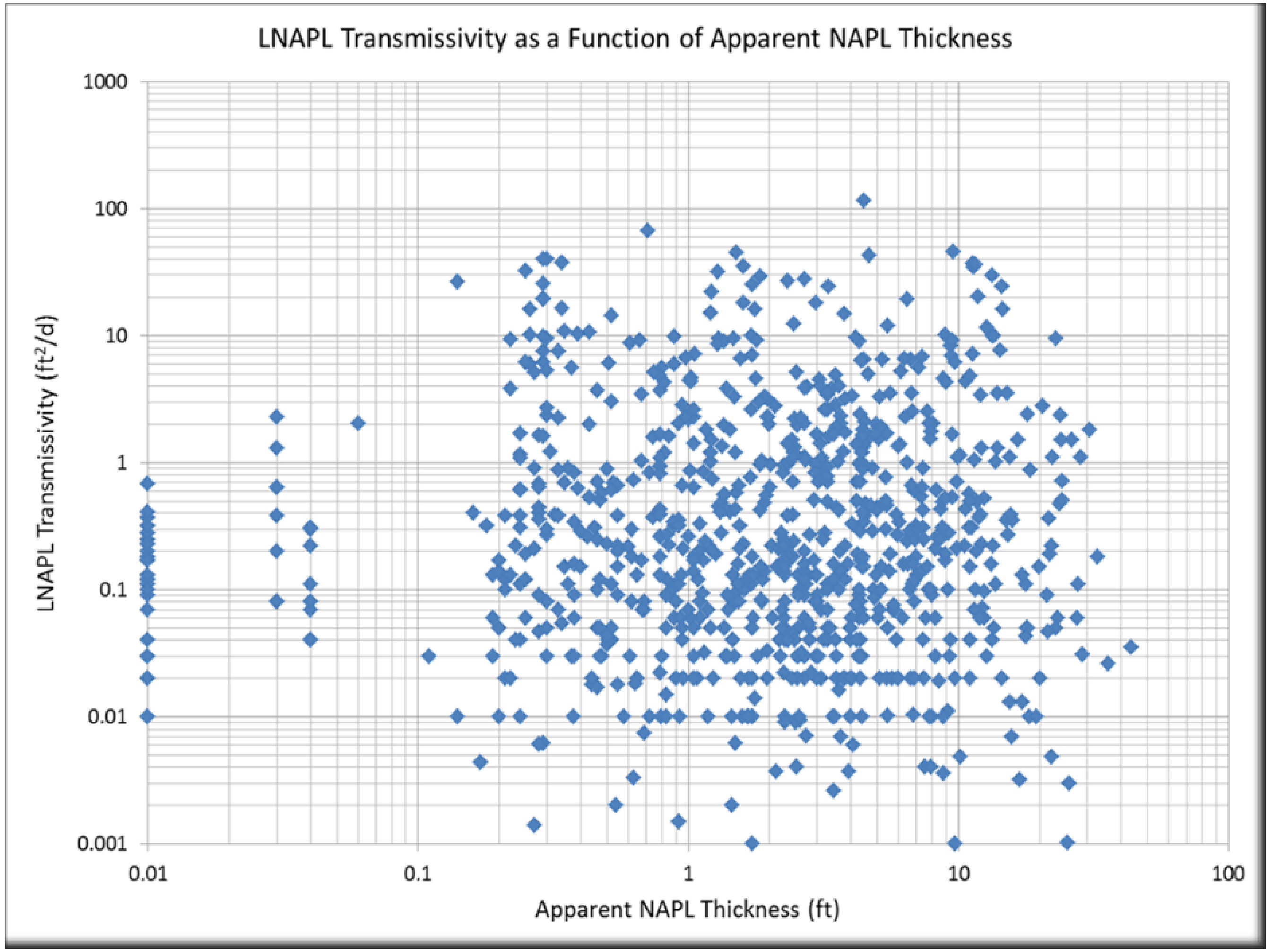
LNAPL Concepts

Parameter	Potential lines of evidence
Stability	LNAPL age (time since release)
	Well observations
	Trends in dissolved phase extent, dissolved mass, centre of mass location
	LNAPL mobility lines of evidence
	NSZD
Mobility	LNAPL age (time since release)
	LNAPL saturations compared to residual levels
	LNAPL transmissivity
	Recovery system performance
	LNAPL stability lines of evidence
Recoverability	LNAPL transmissivity
	Recovery system performance
	Other LNAPL mobility lines of evidence

Adapted from: CRC CARE Technical Report 46

In-well LNAPL thickness

does not correlate well with LNAPL mobility or recoverability



Hawthorne, J. Michael, Dennis Helsel and Charles Stone (2015) Nationwide (USA) Statistical Analysis of LNAPL Transmissivity (Tn), sponsored by The American Petroleum Institute, (2015 Battelle Bioremediation Symposium)

✱ LNAPL Transmissivity

- Standardized way to assess LNAPL mobility and recoverability
- Based on LNAPL flow into a well

de minimis criteria:

$T_n < 0.8\ ft^2/day$

Designation: E2856 – 13

Standard Guide for Estimation of LNAPL Transmissivity[1]

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 epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This guide provides field data collection and calculation methodologies for the estimation of light non-aqueous phase liquid (LNAPL) transmissivity in unconsolidated porous sediments. The methodologies presented herein may, or may not be, applicable to other hydrogeologic regimes (for example, karst, fracture flow). LNAPL transmissivity represents the volume of LNAPL (L^3) through a unit width (L) of aquifer per unit time (t) per unit drawdown (L) with units of (L^2/T). LNAPL transmissivity is a directly proportional metric for LNAPL recoverability whereas other metrics such as apparent LNAPL thickness gauged in wells do not exhibit a consistent relationship to recoverability. The recoverability for a given gauged LNAPL thickness in a well will vary between different soil types, LNAPL types or hydrogeologic conditions. LNAPL transmissivity accounts for those parameters and conditions. LNAPL transmissivity values can be used in the following five ways: *(1)* Estimate LNAPL recovery rate for multiple technologies; *(2)* Identify trends in recoverability via mapping; *(3)* Applied as a leading (startup) indicator for recovery; *(4)* Applied as a lagging (shutdown) indicator for LNAPL recovery; and *(5)* Applied as a robust calibration metric for multi-phase models (Hawthorne and Kirkman, 2011 (**1**)[2] and ITRC ((**2**)). The methodologies for LNAPL transmissivity estimation provided in this document include short-term aquifer testing methods (LNAPL baildown/slug testing and manual LNAPL skimming testing), and long-term methods (that is, LNAPL recovery system performance analysis, and LNAPL tracer testing). The magnitude of transmissivity of any fluid in the subsurface is controlled by the same variables (that is, fluid pore space saturation, soil permeability, fluid density, fluid viscosity, the interval that LNAPL flows over in the formation and the gravitational acceleration constant). A direct mathematical relationship exists between the transmissivity of a fluid and the discharge of that fluid for a given induced drawdown. The methodologies are generally aimed at measuring the relationship of discharge versus drawdown for the occurrence of LNAPL in a well, which can be used to estimate the transmissivity of LNAPL in the formation. The focus, therefore, is to provide standard methodology on how to obtain accurate measurements of these two parameters (that is, discharge and drawdown) for multi-phase occurrences to estimate LNAPL transmissivity.

1.2 *Organization of this Guide:*

1.2.1 Section 2 presents documents referenced.

1.2.2 Section 3 presents terminology used.

1.2.3 Section 4 presents significance and use.

1.2.4 Section 5 presents general information on four methods for data collection related to LNAPL transmissivity calculation. This section compares and contrasts the methods in a way that will allow a user of this guide to assess which method most closely aligns with the site conditions and available data collection opportunities.

1.2.5 Sections 6 and 7 presents the test methods for each of the four data collection options. After reviewing Section 5 and selecting a test method, a user of this guide shall then proceed to the applicable portion of Sections 6 and 7 which describes the detailed test methodology for the selected method.

1.2.6 Section 8 presents data evaluation methods. After reviewing Section 5 and the pertinent test method section(s) of Sections 6 and 7, the user of this guide shall then proceed to the applicable portion(s) of Section 8 to understand the methodologies for evaluation of the data which will be collected. It is highly recommended that the test methods and data evaluation procedures be understood prior to initiating data collection.

1.3 The values stated in inch-pound units are to be regarded as standard. The values given in parentheses are mathematical conversions to SI units that are provided for information only and are not considered standard.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

1.5 *This document is applicable to wells exhibiting LNAPL consistently (that is, LNAPL transmissivity values above zero). This methodology does not substantiate zero LNAPL transmissivity; rather the lack of detection of LNAPL within the well*

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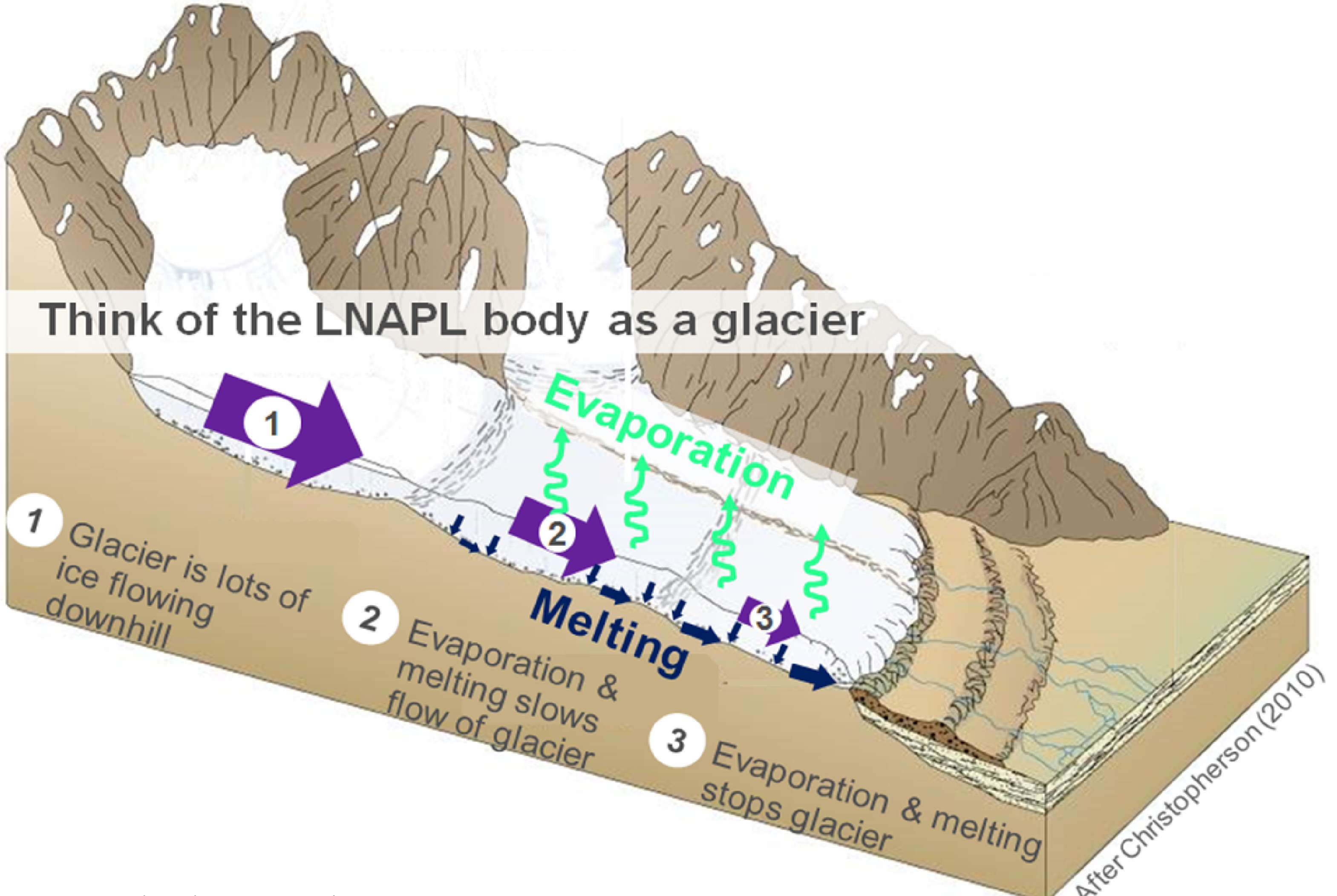
[1] This guide is under the jurisdiction of ASTM Committee E50 on Environmental Assessment, Risk Management and Corrective Action and is the direct responsibility of Subcommittee E50.04 on Corrective Action.

Current edition approved April 1, 2013. Published May 2013. Originally approved in 2011. Last previous edition approved in 2012 as E2856 –12. DOI: 10.1520/E2856–13.

[2] The boldface numbers in parentheses refer to the list of references at the end of this standard.

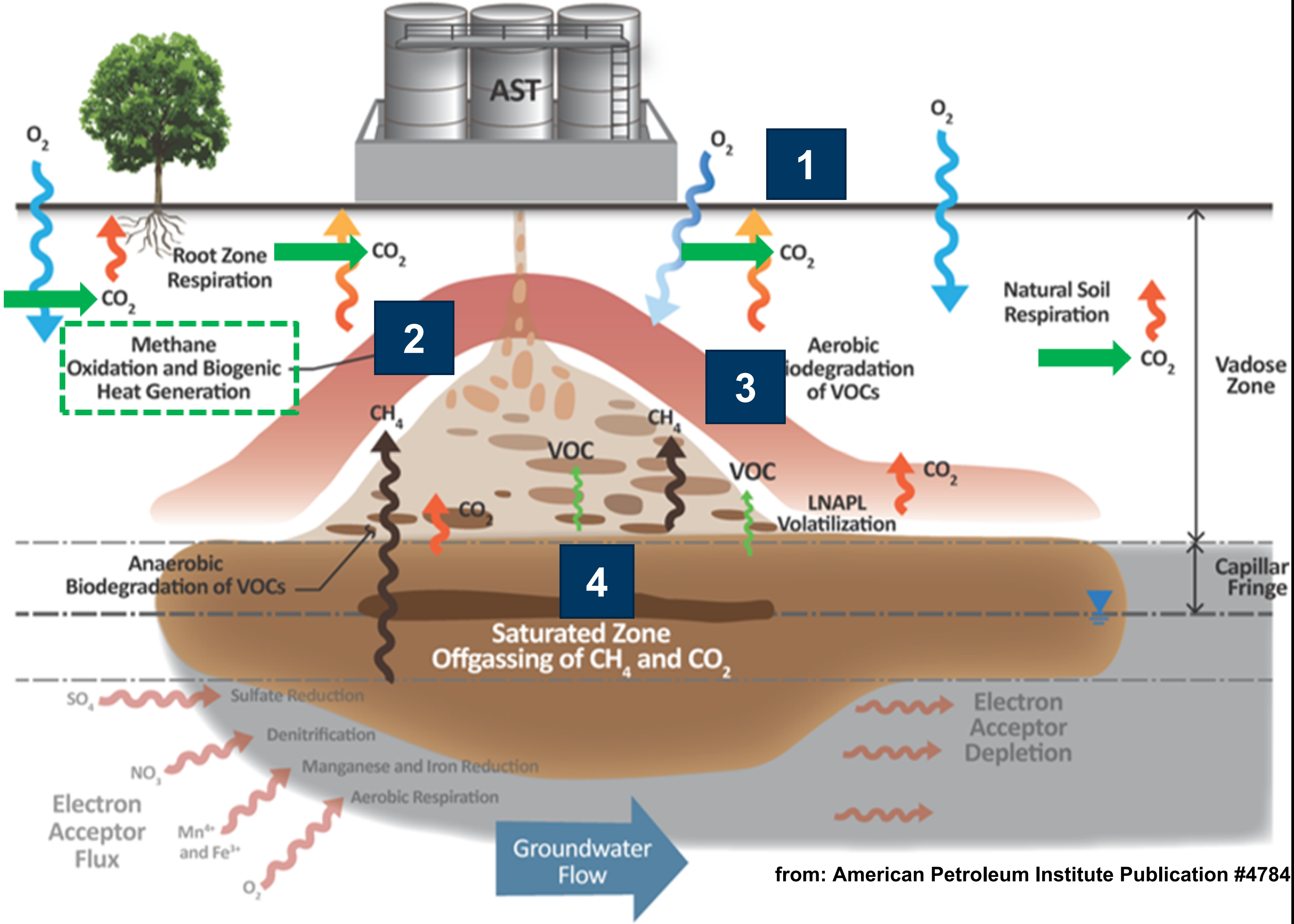
NSZD is a big player in long-term stability



Mahler et al (2012), doi: 10.1111/j.1745-6584.2012.00949.x

- Glacier: melting & evaporation lead to glacier stability/retreat
- Analogously, NSZD leads to LNAPL body stability
- NSZD magnitudes are enough to balance LNAPL gradients

NSZD measurement options



from: American Petroleum Institute Publication #4784

1. Surficial CO_2 Efflux (dynamic closed chamber, CO_2 Trap)
2. Biogenic heat
3. Vertical soil gas gradients (CO_2, O_2, CH_4)
4. Compositional change

Typical NSZD magnitudes

are greater than what is observed in wetlands and less than what is typical at landfills

Representative Degradation Rates from Different Methanogenic Systems

Methanogenic System	Equivalent LNAPL Degradation Rate (Gal/Acre/Year)	Original Measurement	Reference
Anaerobic digesters	500,000	Methane generation[1]	Gerardi 2003
Ethanol release sites	20,000	Carbon dioxide, methane efflux[1]	Sihota et al. 2013
Landfills	10,000	Methane generation[1,2]	Spokas et al. 2006
NSZD at LNAPL sites	2000[3]	Carbon dioxide efflux	Table 3[3]
Wetlands	200	Methane flux to atmosphere[1]	Le Mer and Roger 2001
Peat	4	Methane ebullition[1]	Stamp et al. 2013

1,000 US gallons LNAPL depleted/acre/year

≈ 1 litre LNAPL depleted/m^2/year

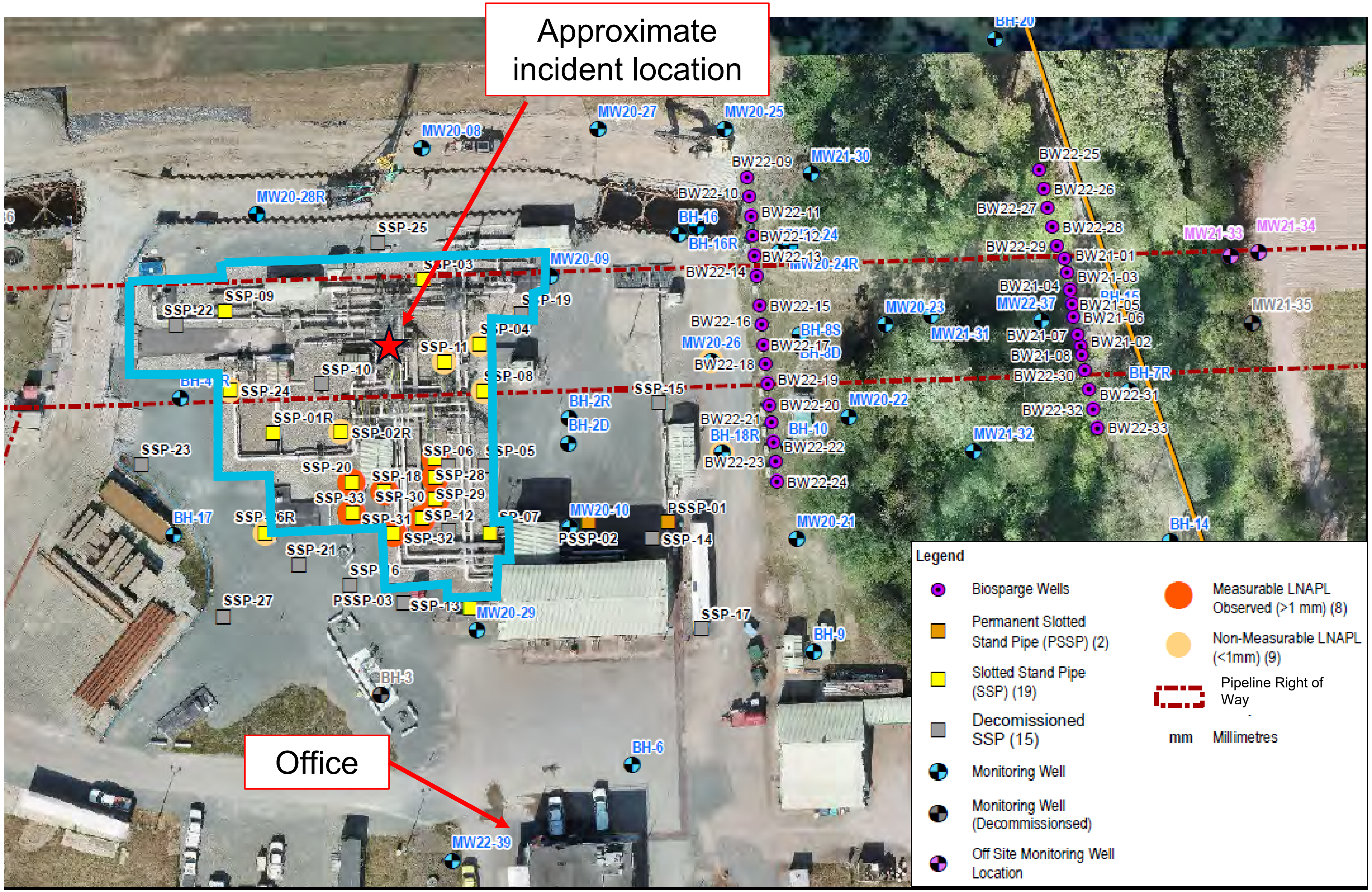
≈ 1 mm depletion in LNAPL thickness/year

Case study

→ Petroleum pipeline release

Pipeline release

- Summer 2020
- 50,000 gallons of crude oil released to ground
- Initial response
  - excavated 20,000 tons impacted soil
  - LNAPL recovery
- July 2021
  - biosparge migration control
  - containment curb
  - engineered liner installed



LNAPL assessment

Things we did:

– Analyze recovery system performance
– Develop LNAPL gauging data plots
– Perform Tn testing
– Characterize LNAPL composition
– Assess LNAPL and dissolved phase stability
– Perform NSZD assessment

Things we did not do:

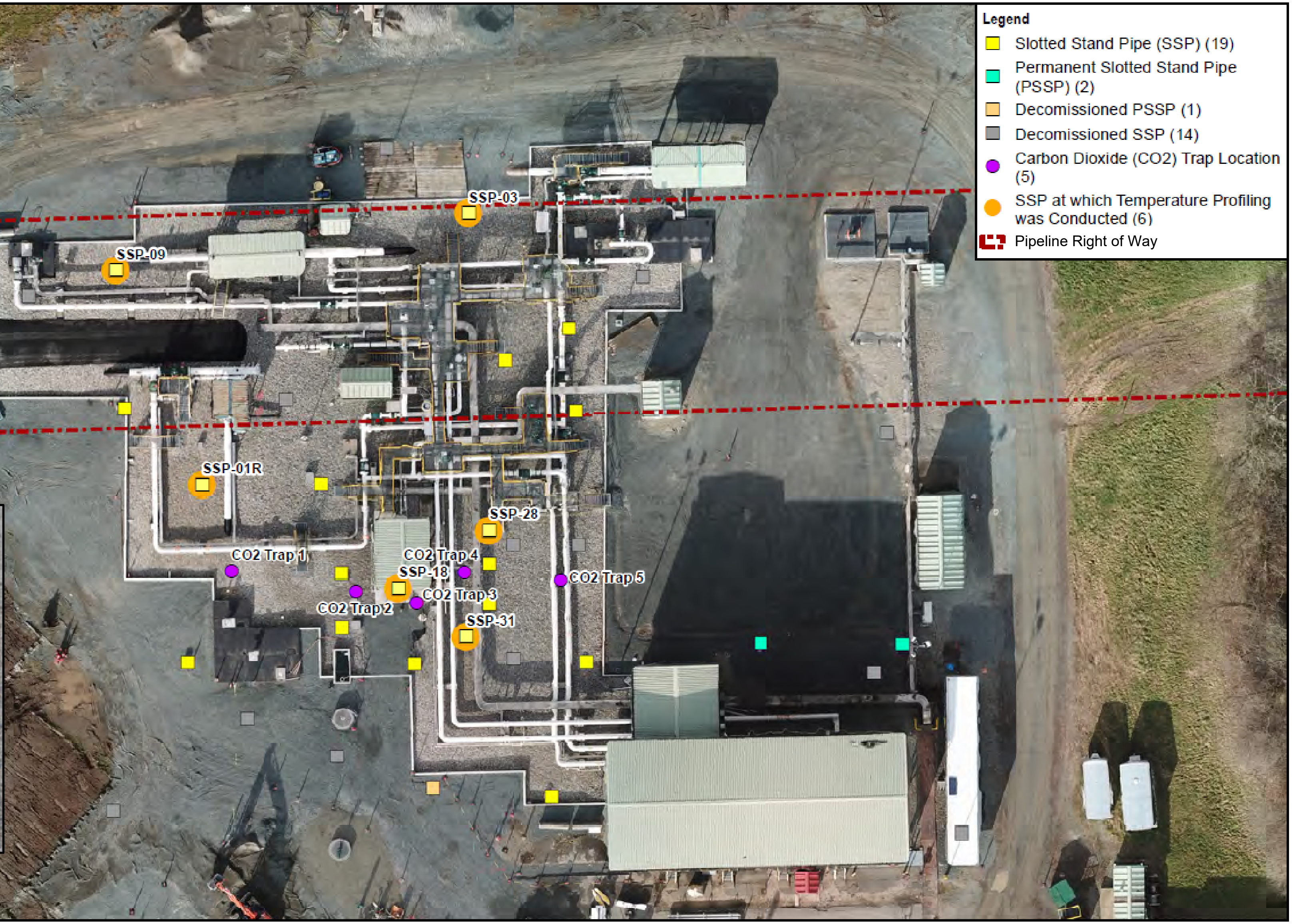
– Produce in-well LNAPL thickness contour plots
– Use in-well LNAPL thicknesses to determine remedial strategies

LNAPL Transmissivity (T_n)

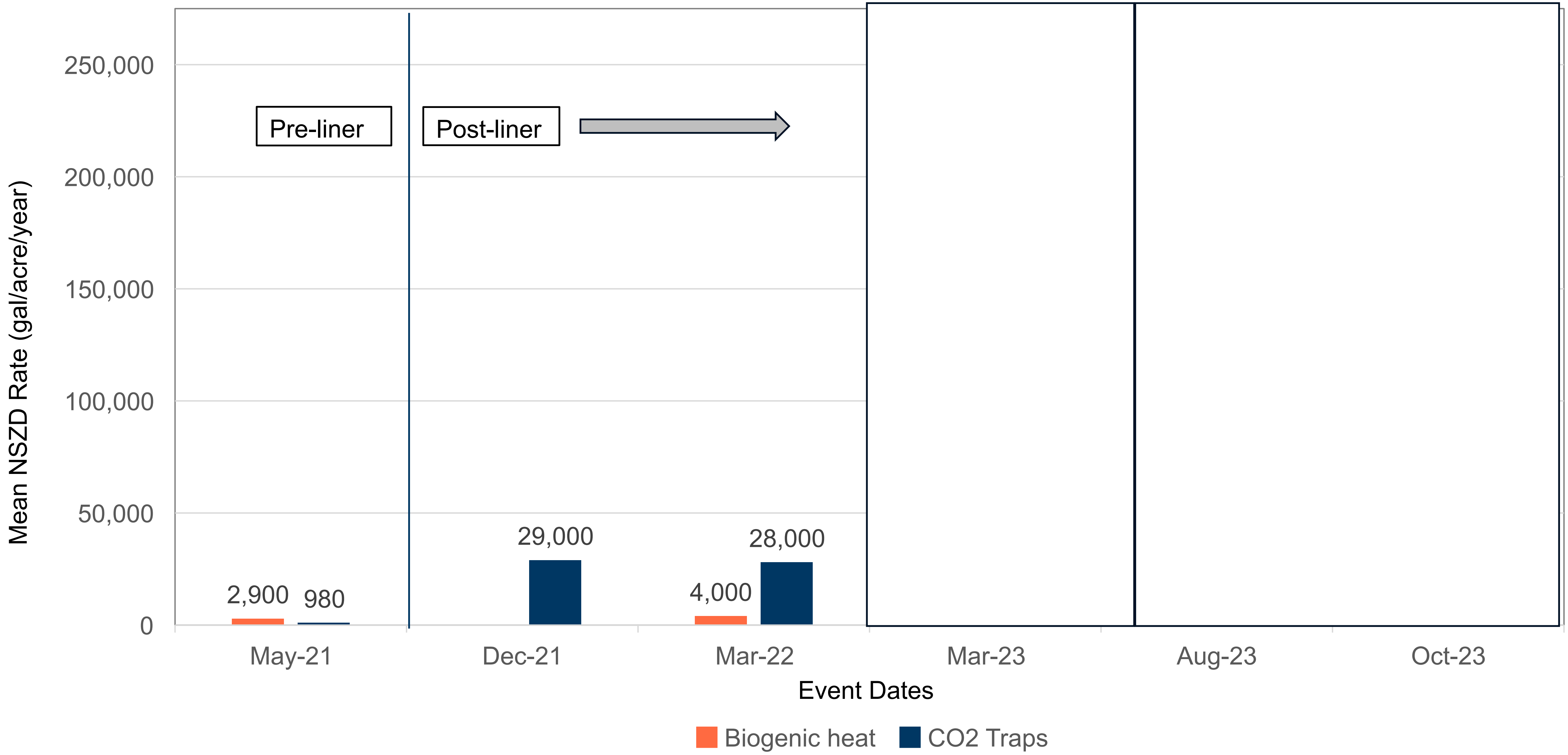
Location	Mean T_n Estimate (ft^2/day)		
	Oct 2020	Mar 2021	Aug 2021
1	0.0		
2	1.0		
3	5.9		
4	3.7		
5	0.4		
6	-		
7	-		

de minimis criteria $T_n < 0.8$ ft^2/day

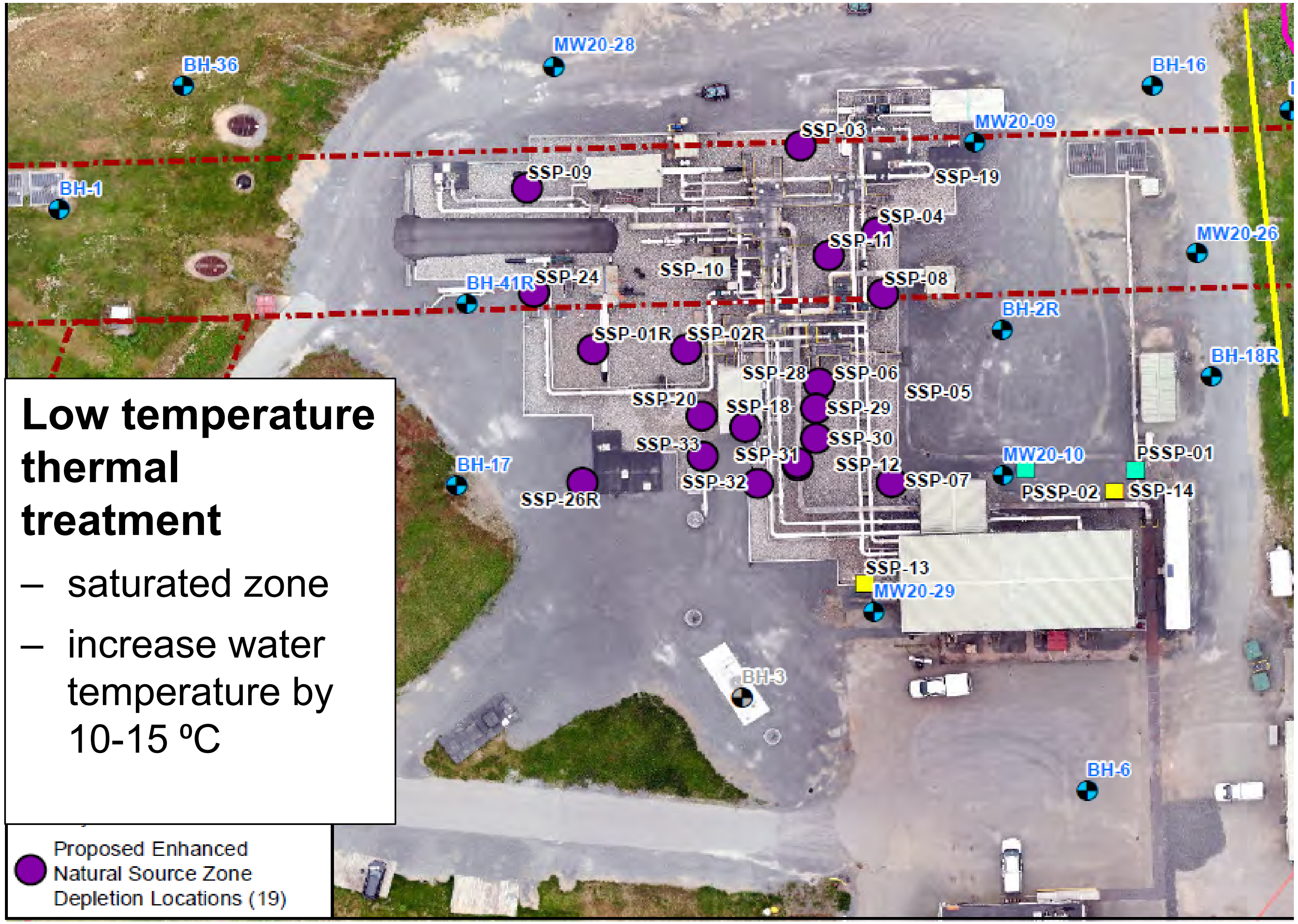
NSZD testing: passive CO_2 traps, biogenic heat



Baseline NSZD Rates

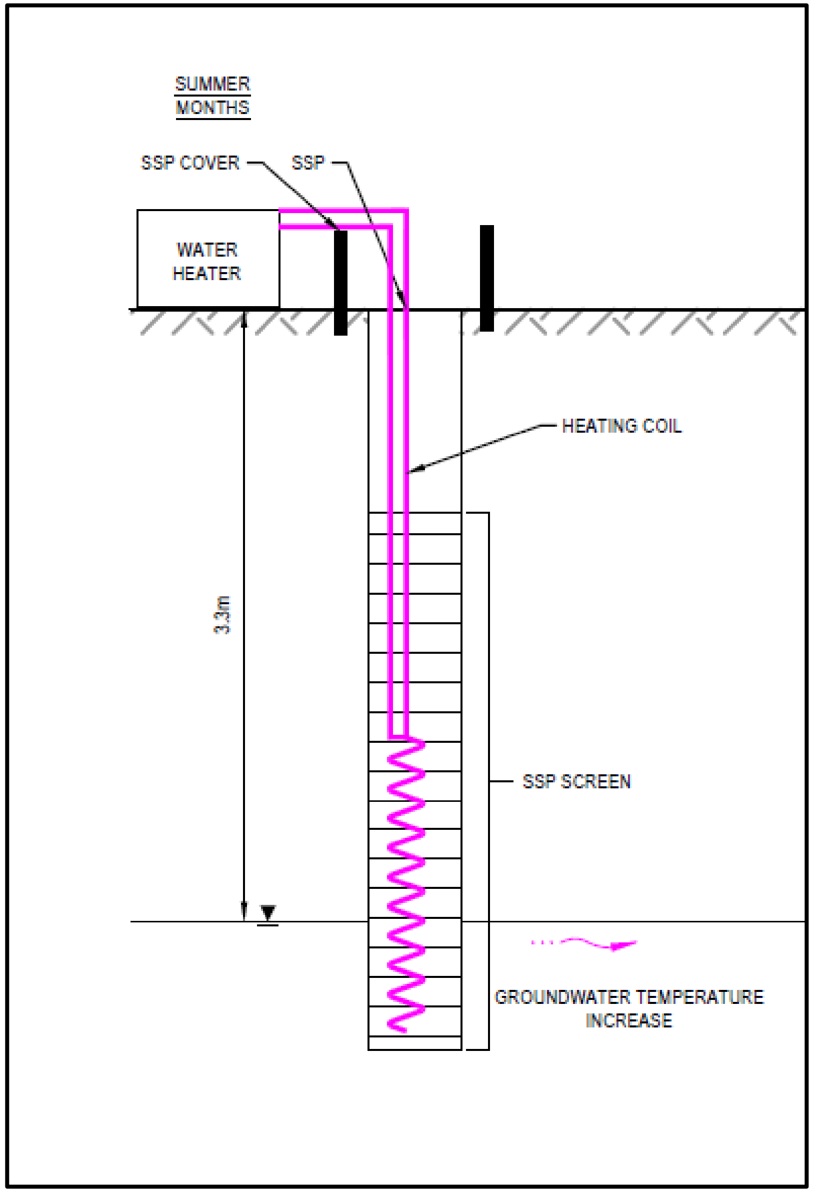


Where are we now? Enhanced NSZD



Low temperature thermal treatment

- saturated zone
- increase water temperature by 10-15 ºC



Keeping the end in mind…

↳ **A transition to a nature-based LNAPL management strategy is considered appropriate when:**

- LNAPL and associated dissolved plumes are stable or in decline
- LNAPL recovery has progressed to a practical end-point
- There is either no risk associated with the remaining LNAPL
  - or-
  any potential exposures can be effectively managed/controlled

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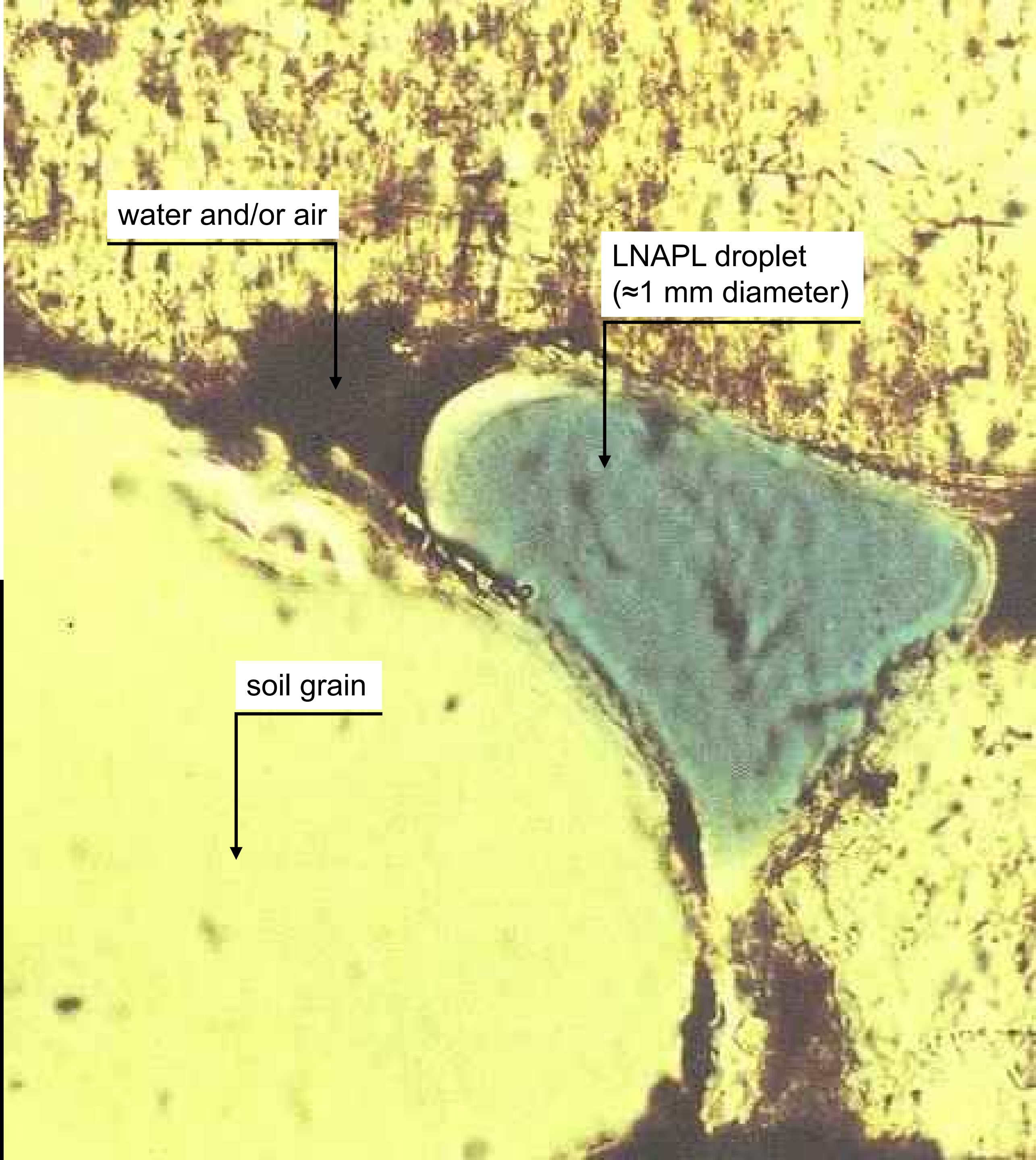
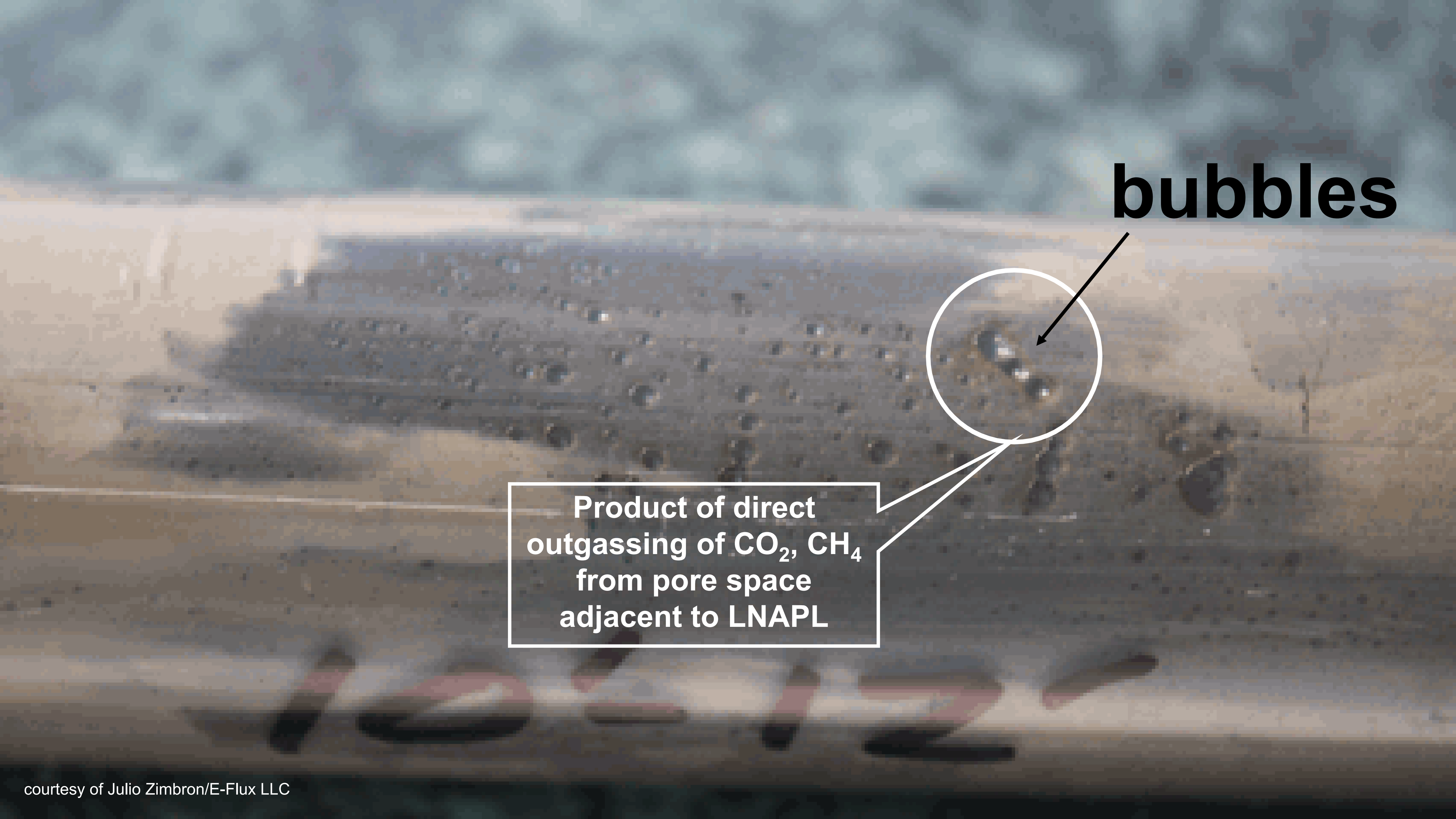
LNAPL saturation: % of pore space filled with LNAPL.

The difference in LNAPL saturation levels that control whether or not LNAPL is observed in a well can be small





courtesy of Julio Zimbron/E-Flux LLC

NSZD Rate Estimate Summary

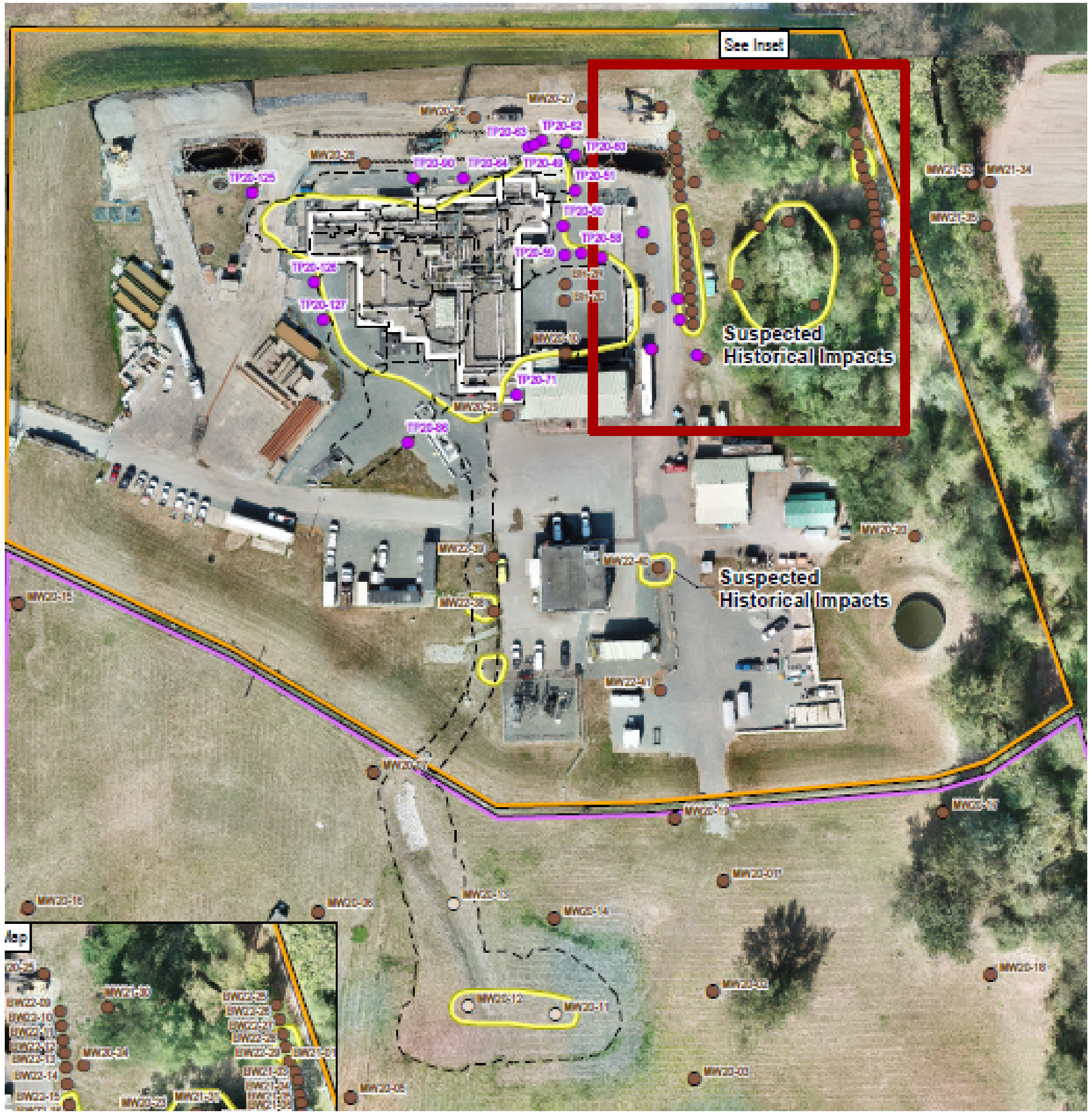
Method	Date	Time frame	Mean NSZD Rate Range (U.S. gal / ac / yr)	Mean NSZD Rate Range (L / m^2 / yr)
CO_2 Traps				
Pre-Liner	May 2021	long-term	980	0.9
Post-Liner	Dec 2021	long-term	29,000	27.4
	Mar 2022	long-term	27,950	26.2
	Mar 2023	long-term	51,250	31.6
	Aug 2023	long-term	176,300	165.0
	Oct 2023	long-term	258,950	242.3
Biogenic heat				
Pre-Liner	May 2021	snapshot	2,900	2.7
	Mar 2022	snapshot	4,000	3.8
Post-Liner	Oct 2023	long-term	6,000	5.6

Technique: Passive CO_2 Traps

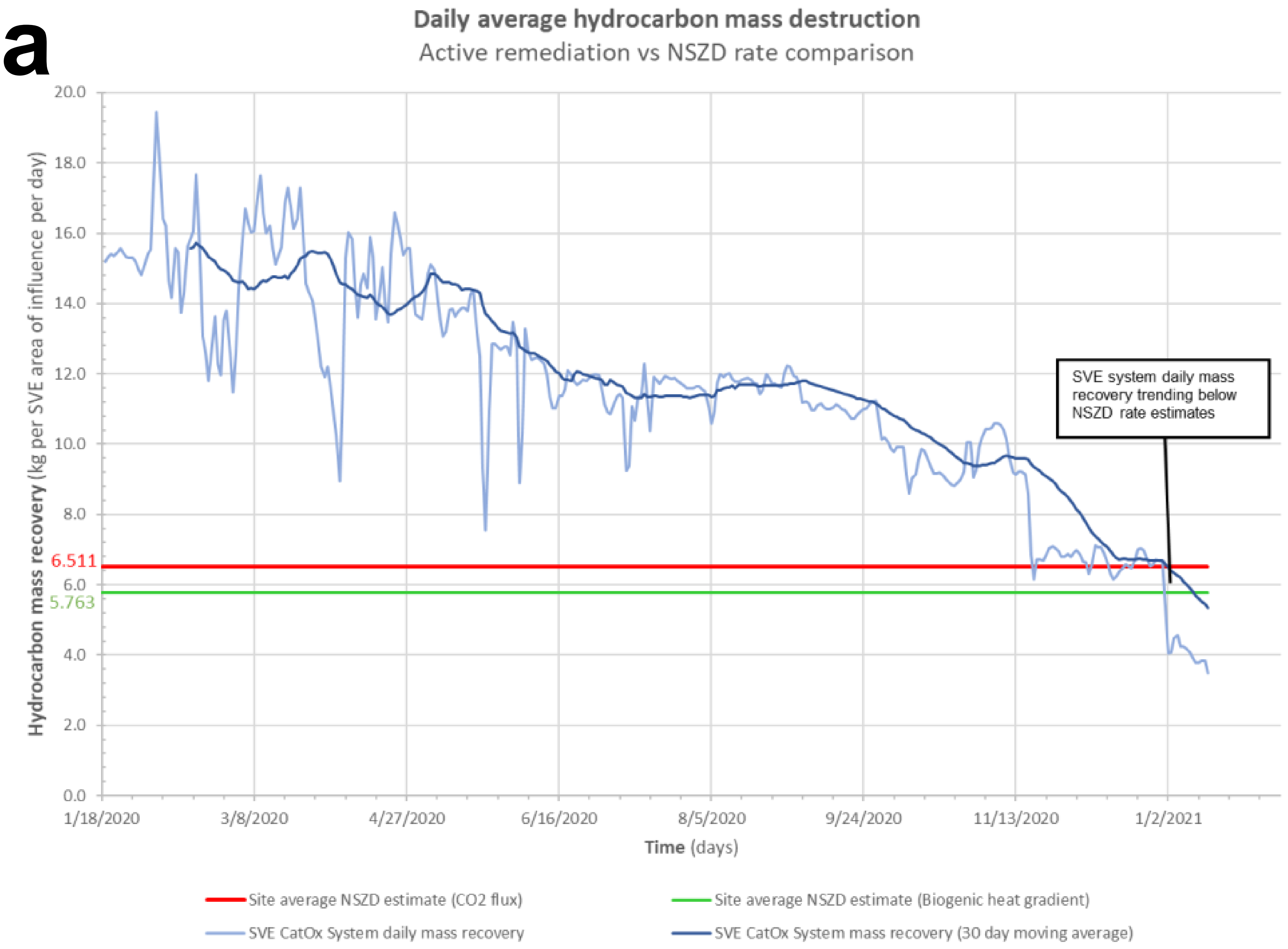
Date	Pre / Post Liner	Deployment Time	CO_2 Trap ID	NSZD rate estimate	
				(U.S. gal LNAPL / ac / yr)	(L LNAPL / m^2 / yr)
May 2021	*Pre-liner*	*6 days*	*Mean*	*980*	*0.9*
Dec 2021	Post-liner	11 days	CO_2-02	35,000	33.2
			CO_2-03	23,000	21.5
Mar 2022	Post-liner	13 days	CO_2-01	27,500	25.7
			CO_2-02	28,400	26.6
Mar 2023	Post-liner	13 days	CO_2-01	35,000*	32.7
			CO_2-02	32,500*	30.4
Aug 2023	Post-liner	2 days	CO_2-01	218,000*	204.0
			CO_2-02	134,600	125.9
Oct 2023	Post-liner	1 day	CO_2-01	397,400*	371.7
			CO_2-02	120,500	112.8

* Trap saturated with carbon

Excavated area



NSZD as a remedial metric



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)

table from Garg et al, 2017 (doi: 10.1111/gwmr.12219)

Most of the action is in the vadose zone