The Shifting Paradigm of Natural LNAPL Biodegradation:

Time to Lose the Pumps?

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October 2019

Agenda

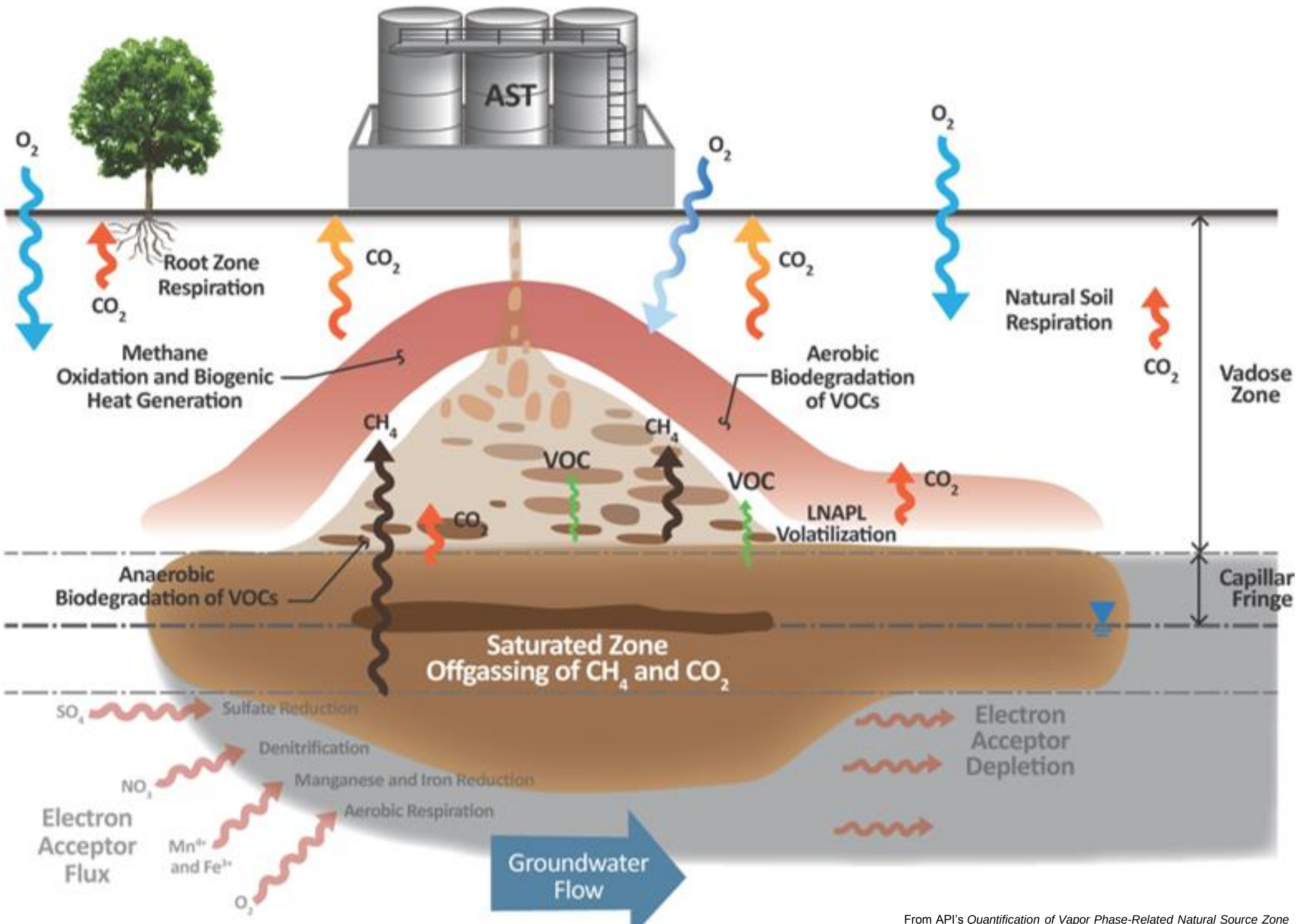
Thought-provoking (presumptuous?) discussion items:

1. NSZD: what is it?
2. NSZD: how is it measured?
3. NSZD vs conventional approaches: things to think about
4. Case studies
5. Questions

NSZD

What is it?

NSZD what is it?



From API's *Quantification of Vapor Phase-Related Natural Source Zone Depletion Processes, First Edition* (API 4784, May 2017)

NSZD what is it?

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)

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.

1,000 US gallons LNAPL depleted/acre/year
≈ 1 litre LNAPL depleted/m^2/year
≈ 10,000 litres LNAPL depleted/ha/year
≈ 1 mm depletion in LNAPL thickness/year

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

Note: All values rounded to one significant figure.
[1]Adjusted to account for CO_2 production (see Appendix S1).
[2]Adjusted to account for oxidized methane in landfill covers (see Appendix S1).
[3]Representative median NSZD rate of about 1700 gallons/acre/year rounded to one significant figure.

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

LNAPL biodegradation: then and now

Item	Hydrocarbon attenuation in the 1990s-2000s	Hydrocarbon attenuation now
Nomenclature	Monitored natural attenuation (MNA) of dissolved plume	Natural source zone depletion (NSZD) of LNAPL body
Management focus	Plume length	Source longevity
Key constituents	Dissolved BTEX	All LNAPL constituents
Key biodegradation process	Electron acceptor mediated biodegradation	Methanogenesis
Key unsaturated zone biodegradation process	Volatilisation of LNAPL followed by aerobic biodegradation of hydrocarbon vapours	Anaerobic biodegradation (methanogenesis) of LNAPL followed by aerobic methane oxidation
Key saturated zone biodegradation process	Anaerobic biodegradation of dissolved BTEX	Anaerobic biodegradation of LNAPL by methanogenesis with off-gassing and ebullition
Key metric	Biodegradation capacity	NSZD rate
Key measurement	Upgradient vs. downgradient electron acceptors and byproducts	CO_2 efflux; gradient of O_2 consumption in vadose zone; thermal flux; compositional change
Representative attenuation rates	BTEX half-life of 2-4 years	NSZD rates of 1,000s to 10,000s L LNAPL ha^{-1} yr^{-1}

adapted from Garg et al, 2017

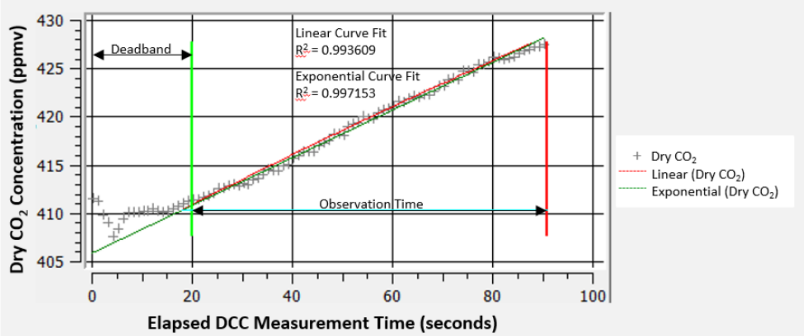
NSZD

How is it measured?

NSZD how is it measured?

Dynamic Closed (Flux) Chamber

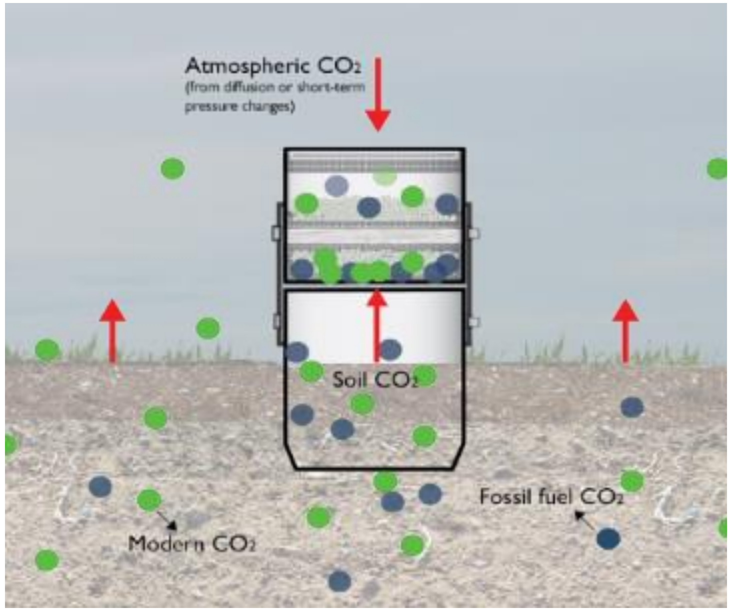
- Active short-term sampling (≈ 15 minutes)
- Measure total CO_2
- Need to correct for background non-LNAPL CO_2 sources (e.g., plant respiration)
  - test locations away from LNAPL
  - ^{14}C CO_2 trap results
- Surface cover can significantly affect results/interpretation
  - vegetated vs. non-vegetated
  - match surface cover types at background locations with LNAPL zone
- Screening tool



NSZD how is it measured?

Passive CO_2 Traps

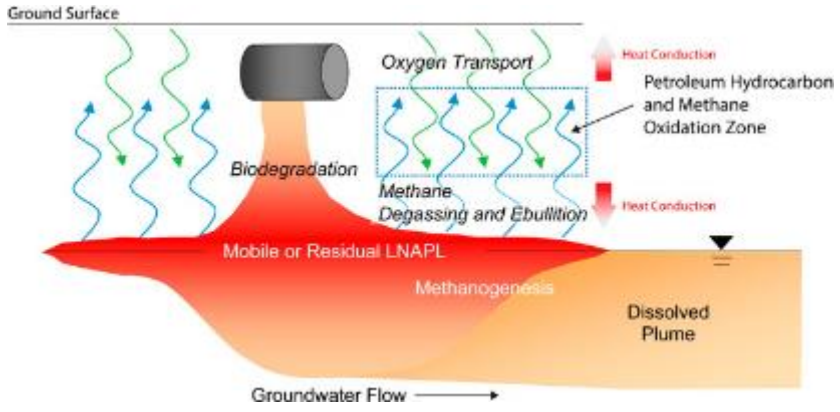
- Passive longer-term sampling (≈ 2 weeks)
- Measure total CO_2, ^{14}C unstable isotope
- ^{14}C analysis provides built-in background correction
  - ^{14}C half-life ≈ 5,600 years
  - modern/background CO_2 is ^{14}C enriched
  - petrogenic CO_2 is ^{14}C depleted
- Best practice = place CO_2 traps based on dynamic flux chamber screening results

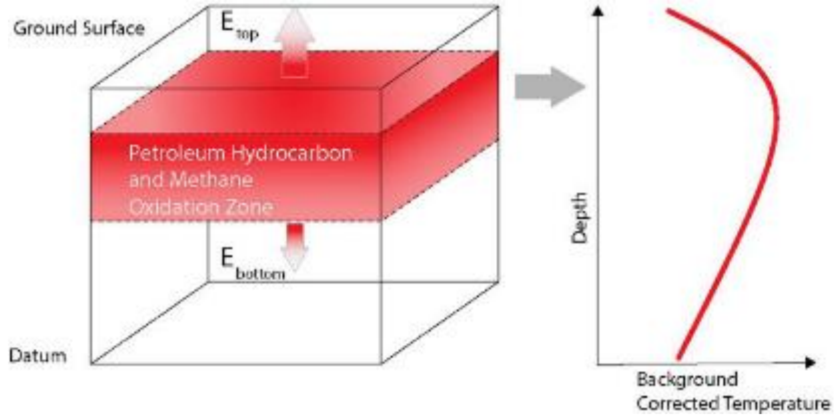


NSZD how is it measured?

Subsurface temperature profiling

- Existing wells or dedicated installations
- Measure temperature at multiple depths through methane-oxidation zone
  - determine temperature gradients up and down
  - heat flux = temperature gradient x thermal conductivity of soil/rock
  - NSZD rate = heat flux / heat of reaction
- Need to correct for background temperatures
  - test locations away from LNAPL

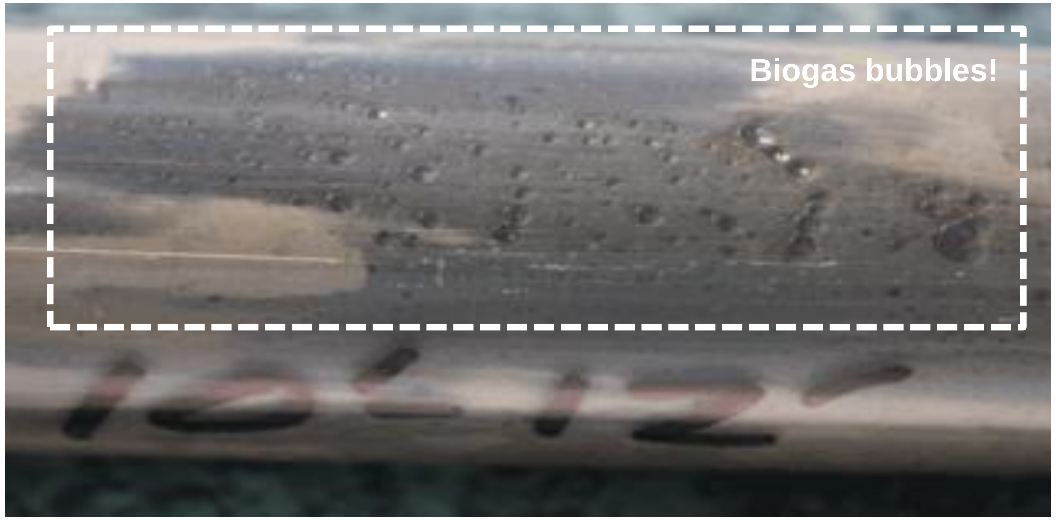




NSZD vs conventional approaches

The things to think about part

NSZD what can it do for us?



Graphic courtesy of Julio Zimbron/E-Flux LLC

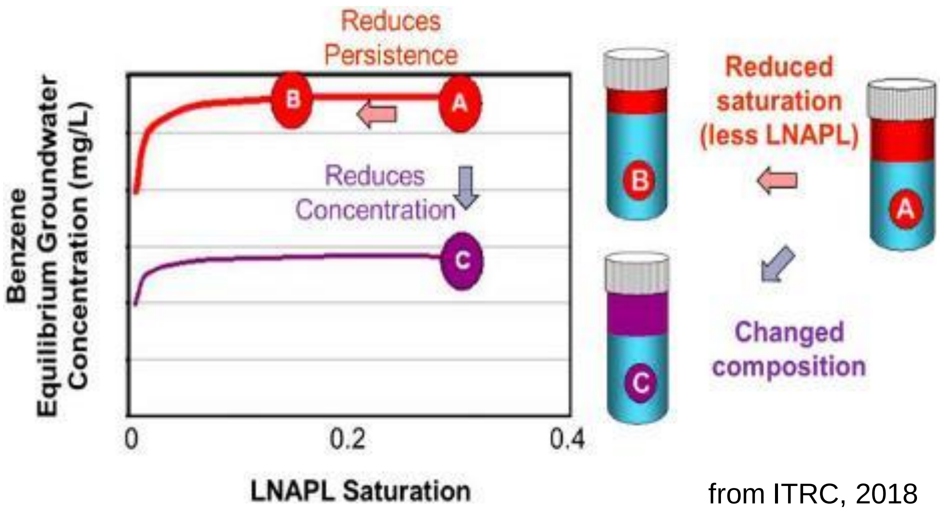
Characterization

- Confirm/quantify active natural attenuation
- Delineate LNAPL footprint
- Supporting line of evidence of LNAPL stability

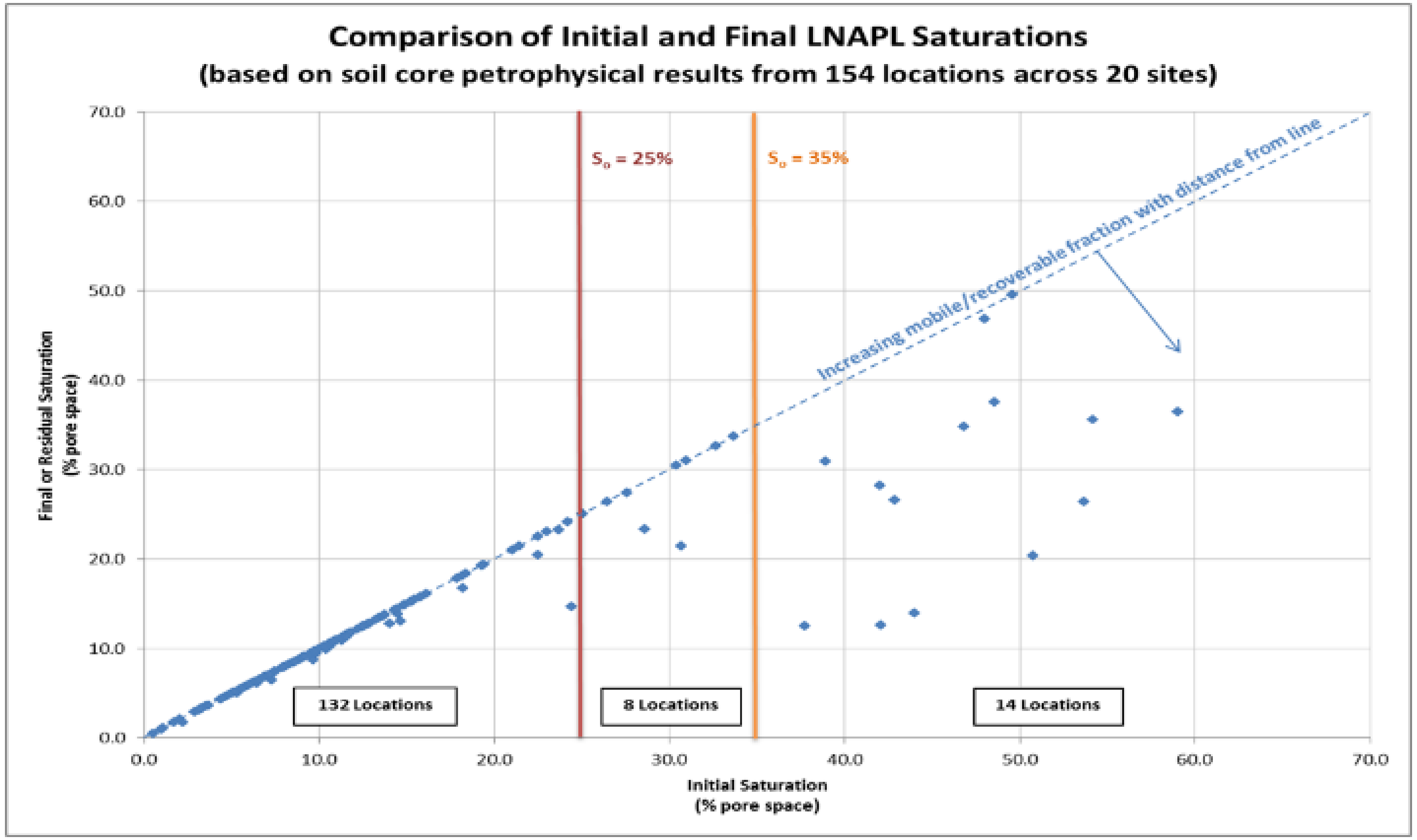
Remediation/Management

- Baseline remedial strategy
  - NSZD rates commonly on the order of 1,000 – 10,000 litres of LNAPL depleted per hectare per year
  - addresses residual LNAPL
- Assessment of net environmental benefit of active remedies
- Performance/MEP metric
- Supporting line of evidence of appropriateness of long-term risk-based LNAPL management

Conventional approaches what can they do for us?



from ITRC, 2018



- Relatively ineffective at reducing saturations into residual range
- Typically ineffective at risk mitigation
- Fractional removal over relatively short-timeframes

Conventional approaches what can they do for us?

MPE system recovering LNAPL at a Superfund site

Item	Quantity
Total LNAPL recovered	394 litres **356 kg**
Average LNAPL recovery rate	0.2 kg/hour
Cost	>$1M >$2,500/litre LNAPL >$2,800/kg LNAPL
GHG emissions – CO_2, CH_4, N_2O (based on electrical power consumption, USEPA eGRID emission factors)	**>150,000 kg** (>100 kg/hour)
Environmental Footprint (based on USEPA SEFA spreadsheets, power consumption, manufacturing of materials, groundwater extraction, etc.)	**143,000 kg CO_2e** **7,300 kg NO_x+SO_x+PM** **20 kg HAPs**

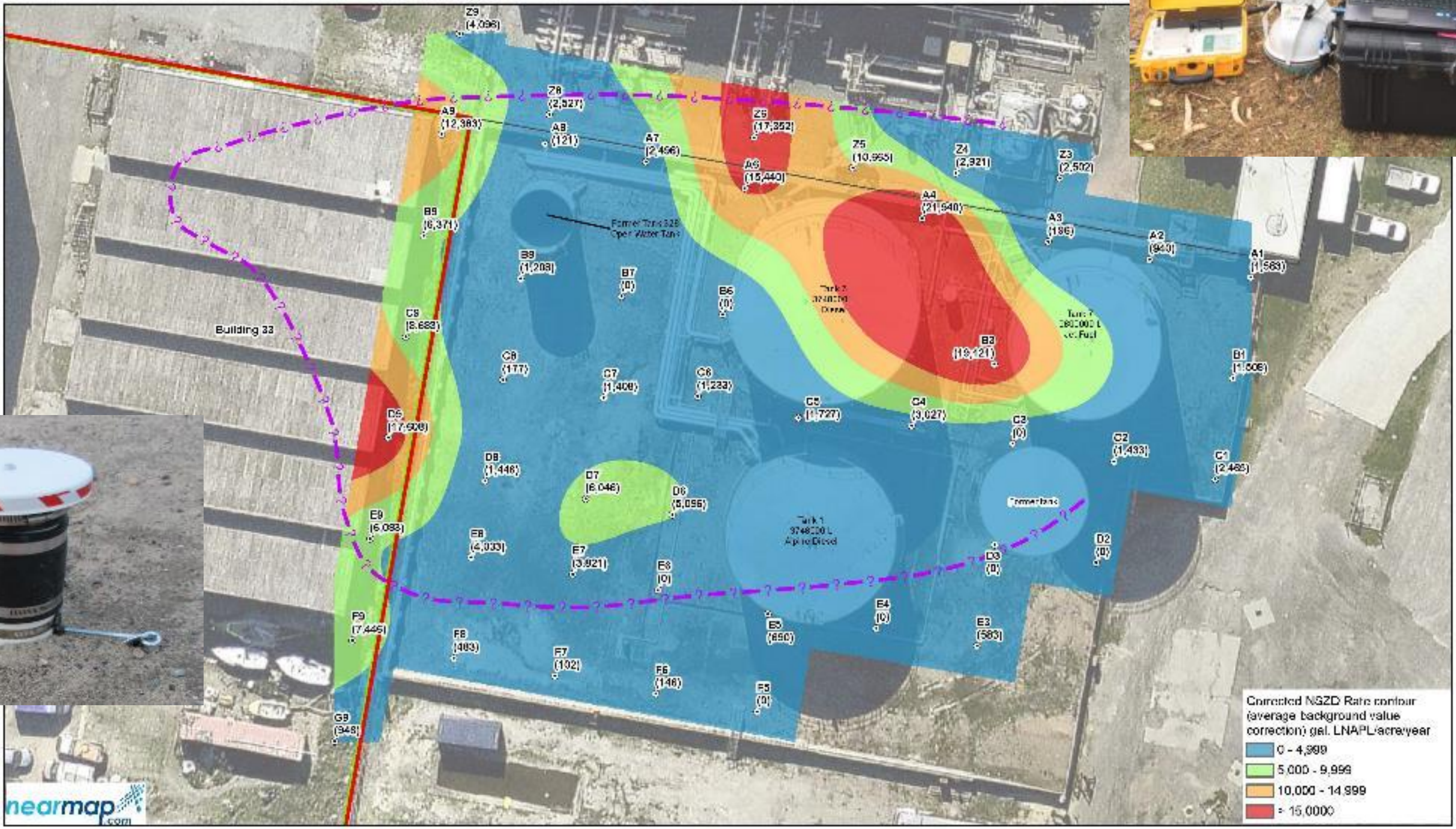
NSZD vs conventional

Consideration	NSZD	Conventional
acts on residual LNAPL?	**yes**	**limited**
depletes LNAPL mass?	yes (mobile + residual)	yes (mobile only)
reduces LNAPL saturations?	yes (mobile + residual)	yes (mobile only)
reduces flux to dissolved/vapour phases?	yes	limited
environmental costs?	**low**	**higher**
remedial risk?	low	higher
$$$	low (maybe)	higher (maybe)

NSZD

Case studies

NSZD case studies *Australia*



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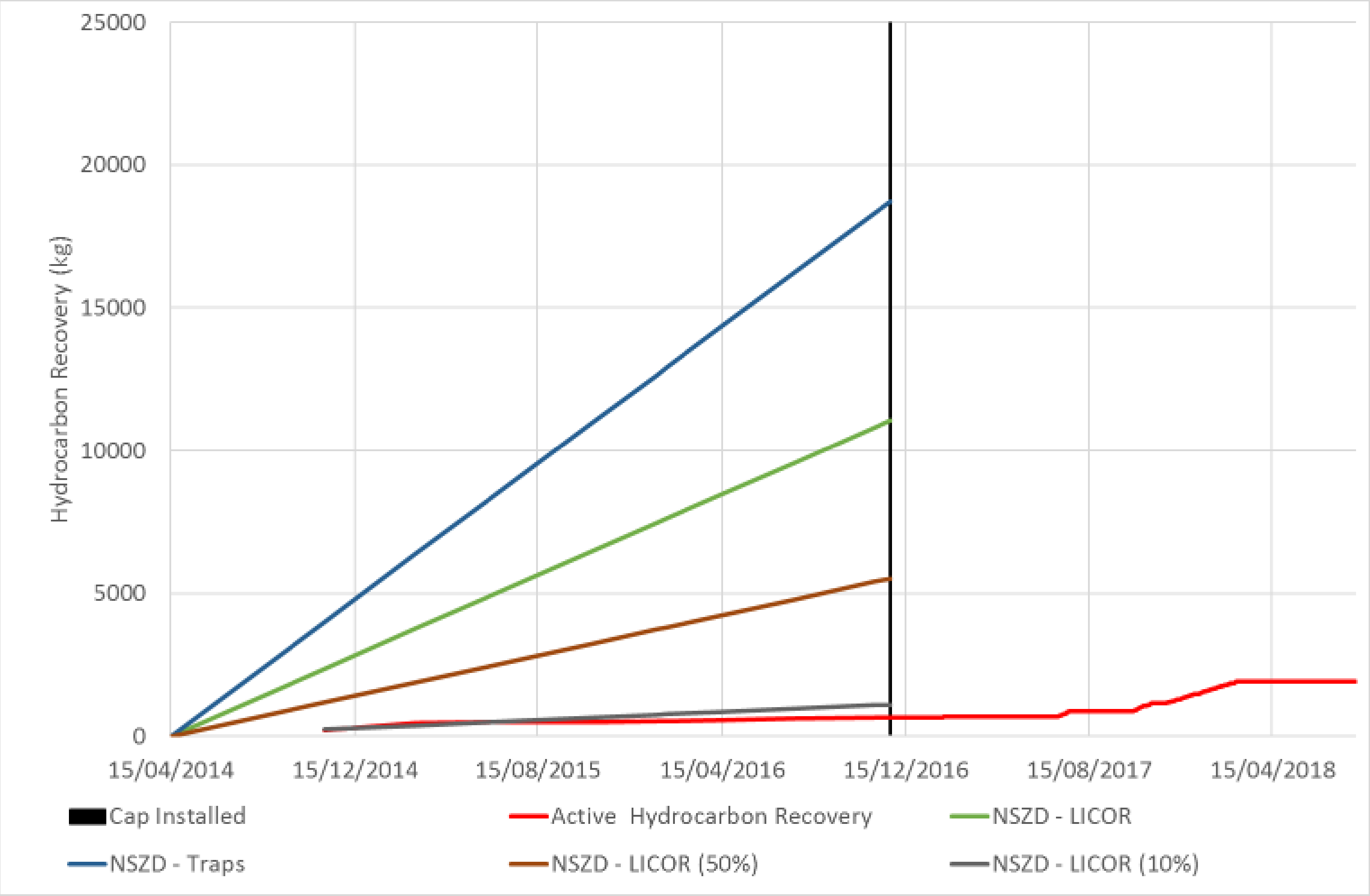
NSZD case studies *Australia*

Location	Flux Chamber NSZD Rate Estimate (L LNAPL ha^{-1} yr^{-1})	CO_2 Trap NSZD Rate Estimate (L LNAPL ha^{-1} yr^{-1})
A6	144,000	145,000
A9	116,000	125,000
B3	179,000	21,000
B7	0	10,000
D7	56,000	9,000
D9	164,000	73,000

NSZD case studies *Australia*



NSZD case studies *Australia*

Biogenic Heat NSZD Rate Estimates

Background (MW29)		*LNAPL Zone (MW24)*			*LNAPL Zone (MW26)*		
Depth (m bgs)	Temperature (°C)	Depth (m bgs)	Temperature (°C)	Background-Corrected Temperature (°C)	Depth (m bgs)	Temperature (°C)	Background-Corrected Temperature (°C)
0.0	22.9	0.0	22.4	-0.5	0.0	23.2	0.3
8.0	23.5	8.0	24.7	1.2	8.0	25.5	2.0
10.0	23.4	10.0	24.4	1.0	10.0	25.1	1.7
10.3	23.3	10.3	24.3	1.0	10.3	25.0	1.7
10.6	23.3	10.6	24.2	0.9	10.6	24.9	1.6
10.9	23.3	10.9	24.1	0.8	10.9	24.7	1.4
11.2	23.3	11.2	24.0	0.7	11.2	24.5	1.2
11.5	23.2	11.5	23.9	0.7	11.5	24.3	1.1
11.8	23.2	11.8	23.9	0.7	11.8	24.2	1.0
12.1	23.1	12.1	23.8	0.7	12.1	24.1	1.0
12.4	23.1	12.4	23.7	0.6	12.4	24.0	0.9
12.7	23.1	12.7	23.7	0.6	12.7	23.9	0.8
13.0	23.0	13.0	23.6	0.6	12.9	22.9	-0.1
13.3	23.0	13.1	22.9	-0.1			
13.6	23.0						
13.9	22.1						
14.2	22.1						
14.5	22.1						
14.8	22.1						
15.1	22.1						
15.4	22.1						
15.7	22.1						
16.0	22.1						
16.3	22.1						
16.6	22.1						
16.9	22.1						
17.2	22.1						
18.0	22.0						

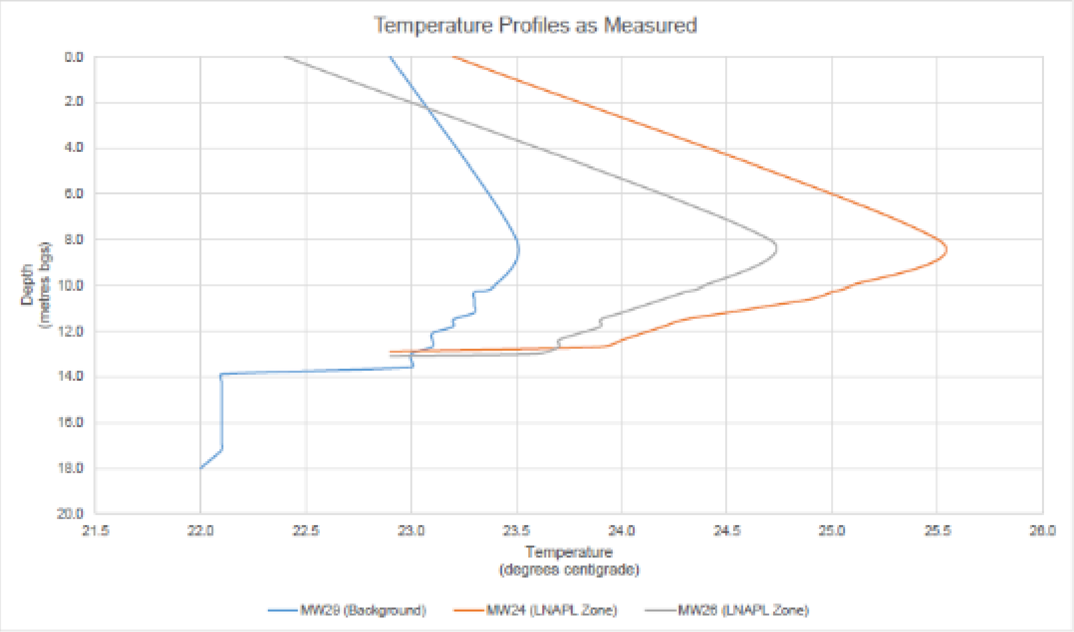
Location	Temp Gradient - dT/dz (C m^{-1})			Heat Flux - q (J m^{-2} s^{-1})	NSZD Rate (g m^{-2} s^{-1})	NSZD Rate (kg ha^{-1} year^{-1})
	Up	Down	Total			
MW26	0.20	0.12	0.32	1.0	0.00002	6374
MW24	0.21	0.26	0.47	1.4	0.00003	9221

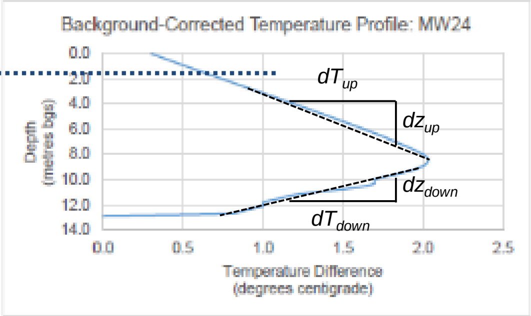
Assumed thermal conductivity (J m^{-1} C^{-1} s^{-1})*	3
Assumed heat of reaction (KJ/g)**	-48

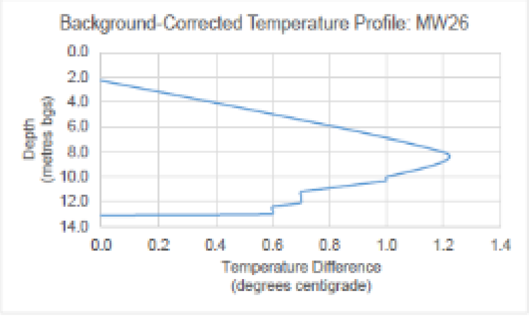
*assumed based on published values for soil/rock
**based on octane (Sweeney & Ririe, 2014)

literature value or laboratory test results

for methane oxidation



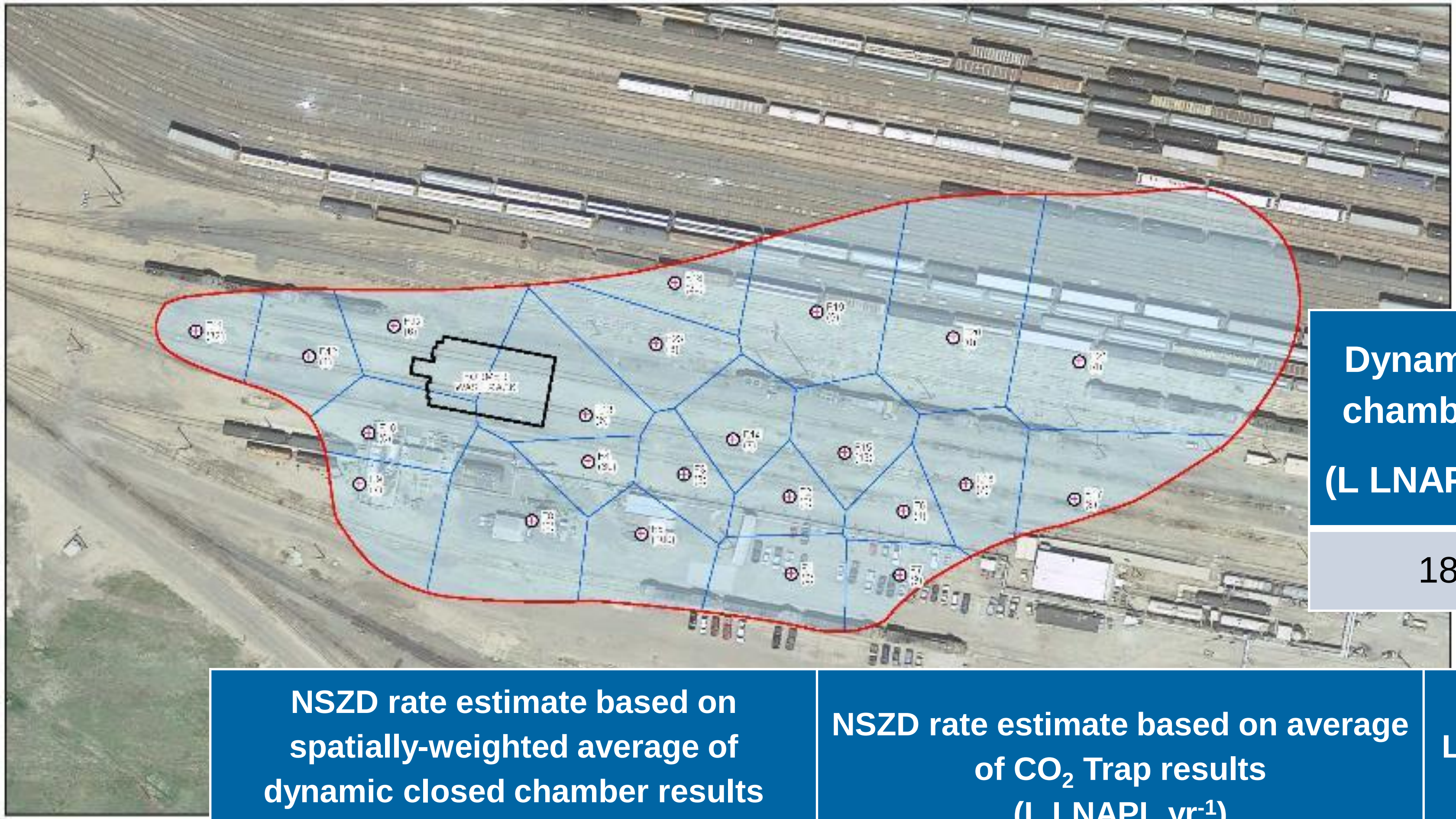




$$q_T = -K_T(\Delta T/\Delta z)_{upward} - K_T(\Delta T/\Delta z)_{downward}$$

$$R_{NSZD} = q_T/\Delta H_{rxn}$$

NSZD case studies *USA*



Dynamic closed chamber results (L LNAPL ha^{-1} yr^{-1})	CO_2 Trap results (L LNAPL ha^{-1} yr^{-1})
187,000	120,000

NSZD rate estimate based on spatially-weighted average of dynamic closed chamber results (L LNAPL yr^{-1})	NSZD rate estimate based on average of CO_2 Trap results (L LNAPL yr^{-1})	LNAPL recovery performance history (L LNAPL yr^{-1})
130,000	15,000	2018: 5,000 2017: 13,000

Questions

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