



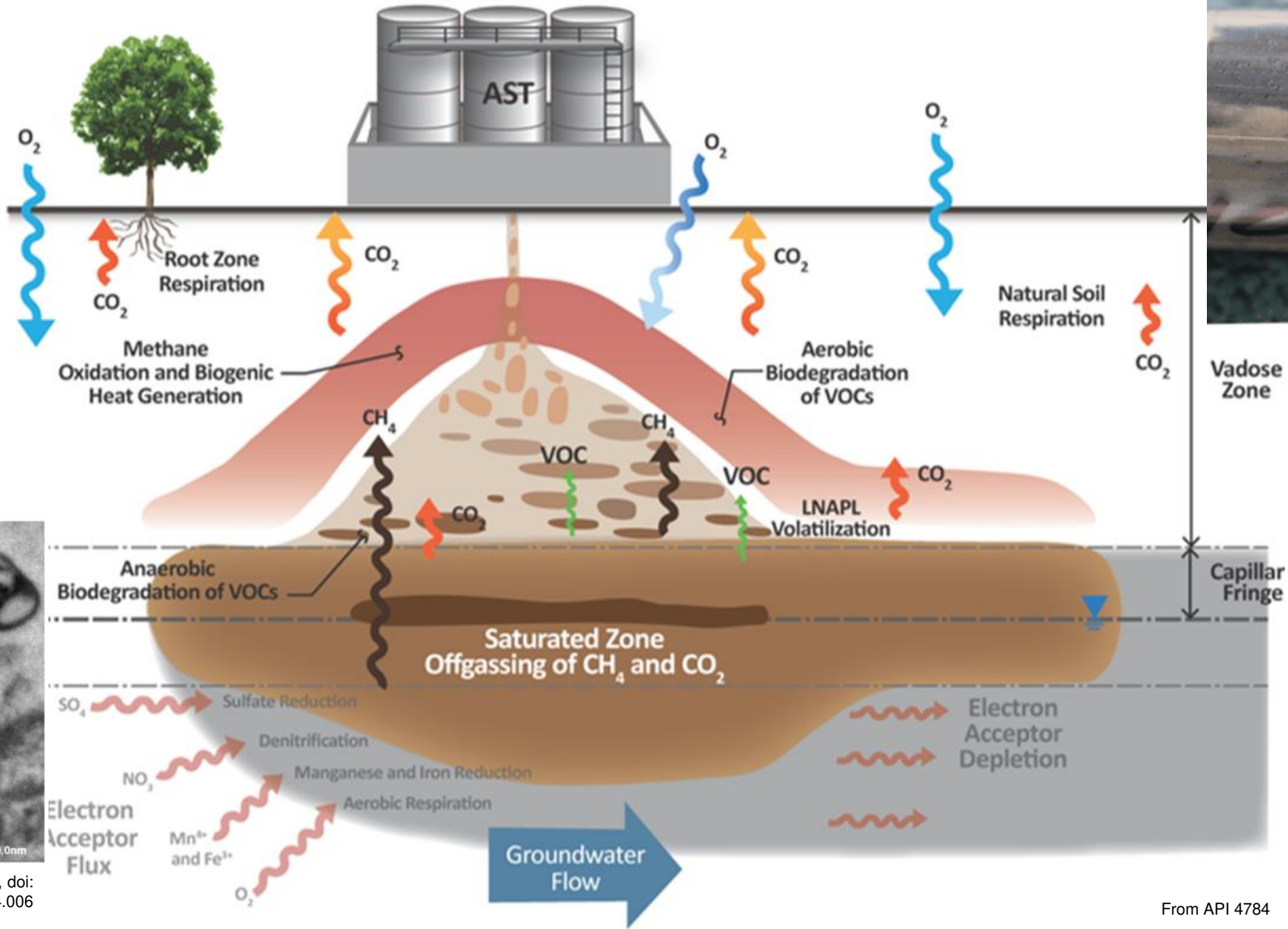
NSZD of DNAPL: Is it a Thing?

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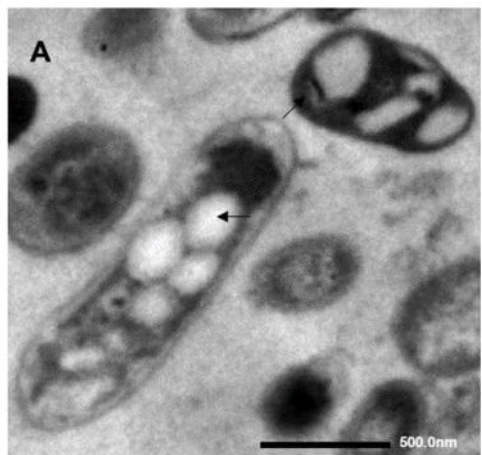
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NSZD with LNAPL



Courtesy of E-Flux LLC



from Ng et al, 2014, doi: 10.1016/j.jconhyd.2014.04.006

Introduction

Research on natural source zone depletion (NSZD) for petroleum, light nonaqueous-phase liquids (LNAPLs) has led to the development of several industry-accepted methods for quantifying natural LNAPL depletion rates. Like petroleum LNAPLs, coal tar and creosotes are composed of complex mixtures of hydrocarbon compounds. Creosotes are denser than water (DNAPLs), but are subject to the same natural depletion mechanisms (i.e., volatilization, dissolution, and biodegradation) as petroleum hydrocarbons and methods for quantifying NSZD rates at petroleum LNAPL sites are applicable for creosote DNAPL sites.

NSZD was assessed at a former tie treating facility where creosote is present in the subsurface related to historical wood treating operations. NSZD rates were determined using a multiple lines of evidence approach to evaluate and quantify NSZD rates, including 1) analysis of groundwater data; 2) measurement of carbon dioxide flux at ground surface;

Site Background

- Former tie treating facility operated from early 1900s to 1980s
- All former facility structures razed in 1980s
- Biosparging system protective of off site groundwater quality since middle 2000s
- NSZD evaluated for source zone areas upgradient of sparging system

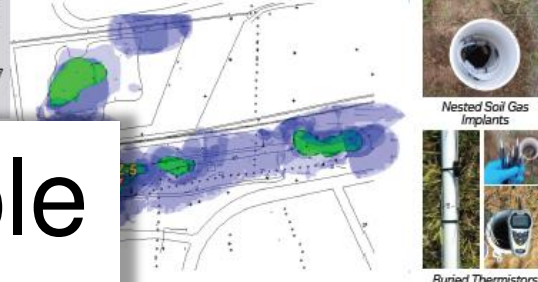
Evidence of NSZD from Groundwater Data



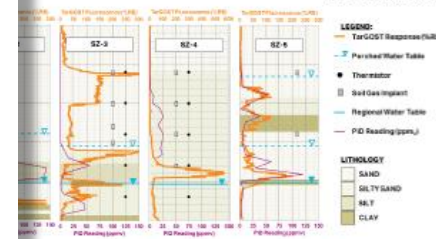
MEASURED PARAMETER	BACKGROUND WELLS	SOURCE ZONE WELLS
GRO	<0.1	2.7
DRO	<0.11	8.0
O ₂	7.8	2.0

2017 Supplemental Evaluation

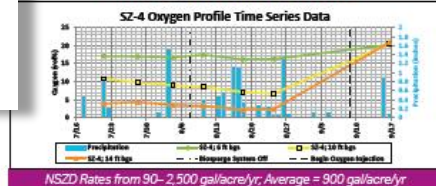
- Permanent nested soil gas implants and temperature probes installed at 5 locations
- Soil gas and temperature data recorded weekly in July-August 2017
- Respiration testing in September-October 2017



Average NSZD rates from multiple measurement techniques in the 100s of US gal/acre/year or 1000s L/ha/yr

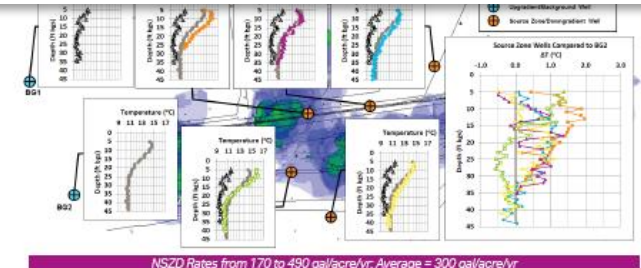
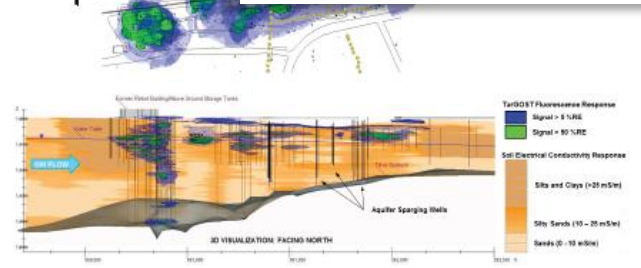
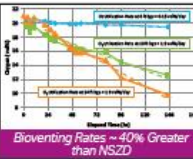


Gradient Method Results



Summary

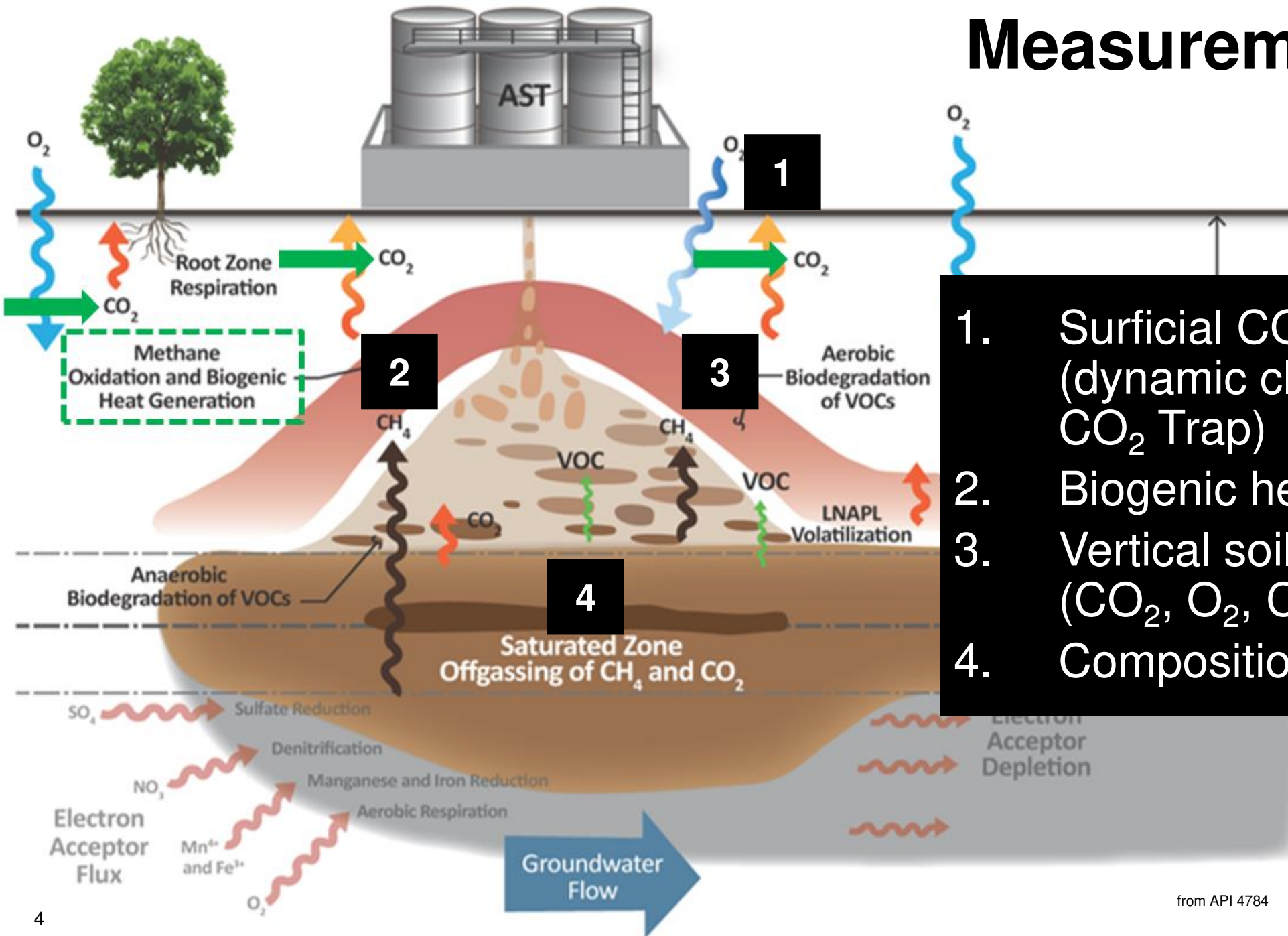
- NSZD rates evaluated using multiple approaches, and results for each method demonstrate that NSZD is occurring, with relative agreement between methods.
- NSZD rates for this creosote site are significant compared to active remediation approaches.
- Mass depletion rates estimated based on respiration test results indicate that bioventing has limited potential to enhance biodegradation rates.



NSZD Rates from 170 to 490 gal/acre/yr, Average = 300 gal/acre/yr

NSZD Rates from 90-2,500 gal/acre/yr, Average = 900 gal/acre/yr

Measurement options



from API 4784

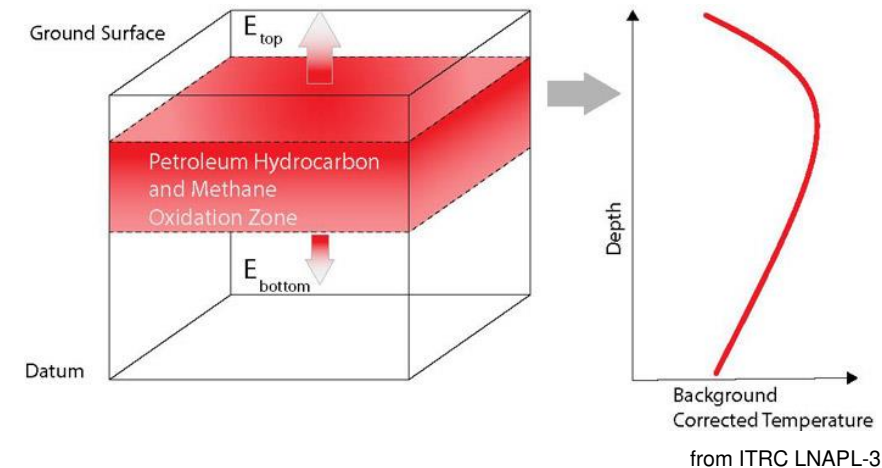
Technique 1: dynamic closed chamber

- Active short-term sampling (≈ 5 minutes)
- Correct for background non-LNAPL CO_2 sources (e.g., plant respiration) using test locations away from LNAPL
- Surface cover can significantly affect results and interpretation
 - vegetated vs. non-vegetated
 - match surface cover types at background locations with LNAPL zone



Technique 2: biogenic heat

- 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 (e.g., **CH₄ oxidation = 48 kJ/g C₁₀H₂₂**)
- Correct with background locations of modelled background profile

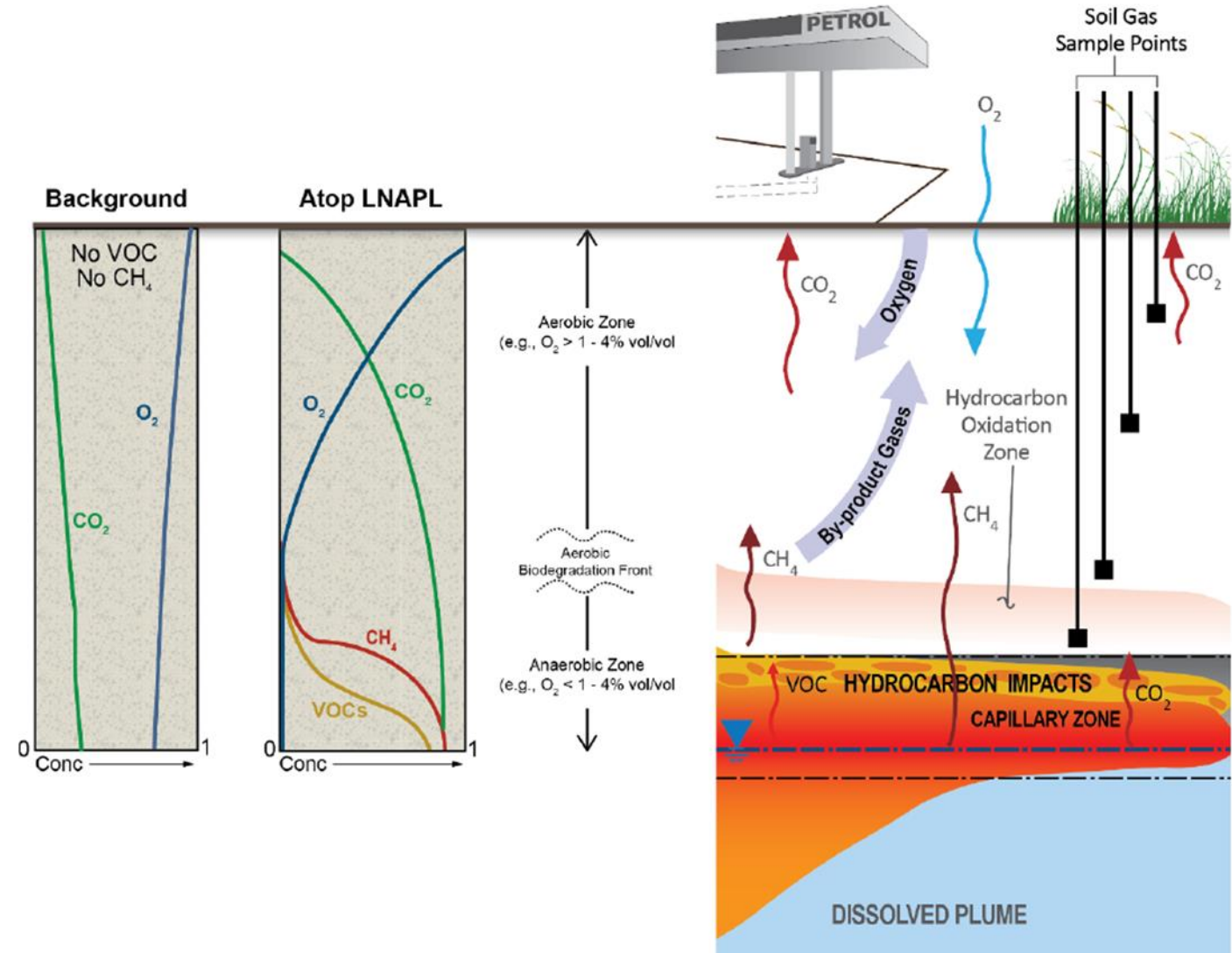


Technique 3: soil gas gradient

Fick's Law

$$[\text{Diffusive } O_2 \text{ flux, } J] = [\text{O}_2 \text{ concentration gradient}] \times [\text{diffusivity, } D_v]$$

$$0.3g \text{ C}_8\text{H}_8 \text{ (LNAPL)}/g \text{ O}_2$$



from CRC CARE Technical Report 44

The test site

— Former MGP site with coal tar DNAPL

The site – former MGP



Groundwater Monitoring Well		Preliminary subsurface gas and biogenic heat monitoring locations		Inferred NAPL extents		Soil gas flux monitoring locations	
	On-Site well		Preliminary subsurface gas and biogenic heat monitoring location		DNAPL Extent		DCC monitoring location above DNAPL plume
	On-Site well (missing)		Preliminary subsurface gas monitoring location		Current LNAPL Extent		DCC monitoring location above LNAPL plume
			Off-Site Well		Historical LNAPL Extent		DCC monitoring location in background location

Technique 1: dynamic closed chamber

Location code	Surface cover	Soil Type	Total Number of observations	Raw CO ₂ Flux (μMol/m ² /s)	Corrected CO ₂ Flux (μMol/m ² /s)	NSZD rates based on Corrected CO ₂ flux (L DNAPL/ha/yr)
Background Locations						
BCC01	Vegetation		4	4.4389		
DDCC22	little to no vegetation		6	1.3944		
DNAPL Plume						
DDCC05	little to no vegetation	Gravel	6	3.5091	2.1147	9,192
DDCC08	little to no vegetation	Silty gravel	5	2.5767	1.1823	5,139
DDCC10	little to no vegetation	Gravelly sand	7	1.9505	0.5561	2,417
DDCC12	little to no vegetation	Gravelly silt	9	7.3927	5.9984	26,072
DDCC15	little to no vegetation	Silty gravel	6	1.2901	0	0
DDCC16	little to no vegetation	Silty gravel	3	3.1943	1.8000	7,824
DDCC17	little to no vegetation	Silty gravel	9	2.0042	0.6098	2,650
DDCC18	little to no vegetation	Silty gravel	3	2.4755	1.0811	4,699
DDCC19	little to no vegetation	Silty gravel	6	0.9966	0	0
DDCC20	little to no vegetation	Silty gravel	9	2.4754	1.0810	4,698
DDCC21	little to no vegetation	Silty gravel	6	1.0299	0	0
MW27	little to no vegetation	Gravelly clay	6	6.0708	4.6764	20,326
MW30	little to no vegetation	Silty gravel	3	4.7797	3.3853	14,714
DDCC13	little to no vegetation	Gravelly silt	9	1.5383	0.1439	625
DDCC14	little to no vegetation	Silty gravel	9	6.2137	4.8193	20,947
DDCC11	Vegetation	Gravelly silt	9	7.6253	3.1865	13,850
DDCC03	Vegetation	Gravelly silt	3	15.9746	11.5358	50,140
DDCC04	Vegetation	Gravelly silt	6	3.0132	0	0
DDCC09	Vegetation	Gravelly silt	6	6.6541	2.2153	9,629
DDCC01	Vegetation	Silt - silty clay	6	6.0125	1.5737	6,840
DDCC02	Vegetation	Silt - silty clay	6	7.2758	2.8369	12,331
DDCC06	Vegetation	Silt - silty clay	3	6.9980	2.5591	11,123
DDCC07	Vegetation	Silt - silty clay	3	9.9191	5.4803	23,820
MW08a	Vegetation	Silty clay	3	16.4099	11.9710	52,032



Technique 2: biogenic heat

Depth (metres bgs)	MW08A (background)	MW30	
		Temperature (°C)	ΔT (°C)
Temperature profiles			
0.5	15.77344579	17.44444241	1.670996612
1	17.22183411	19.19607255	1.974238435
1.5	18.09723435	19.8090903	1.711855958
2	18.4908472	20.04104907	1.550201869
2.5	18.51010876	20.10343715	1.593328388
3	18.48524486	20.18773551	1.702490654
3.5	18.24281612	20.03045257	1.787636449
4	18.09696799	20.06366939	1.966701402
4.5	17.94429603	19.73164276	1.787346729
5	17.824134	19.66546869	1.841334696
5.5	17.65233084	19.45364556	1.80131472
6	17.50006425	-	-

Note: red values are beneath top of fluid in well

Upper temperature gradient

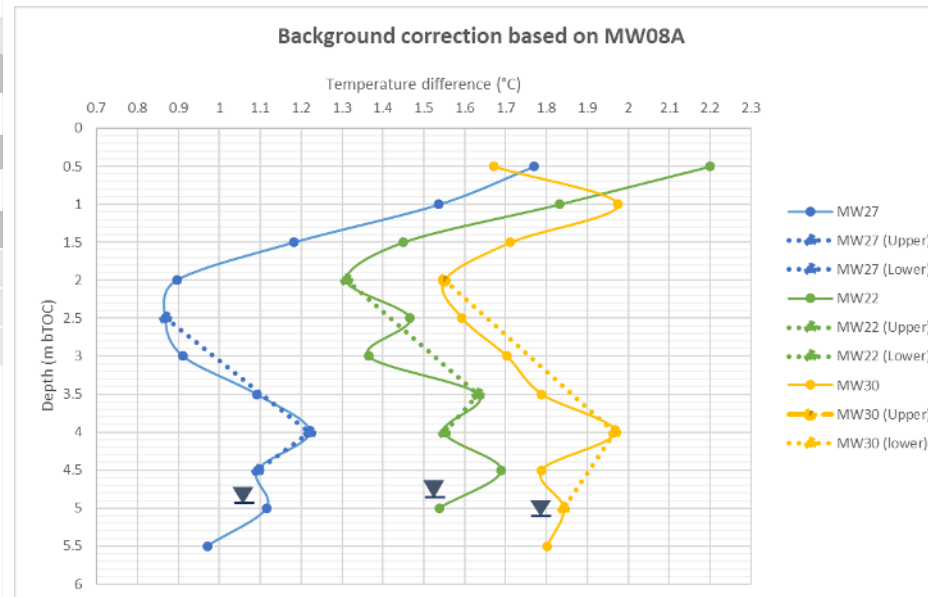
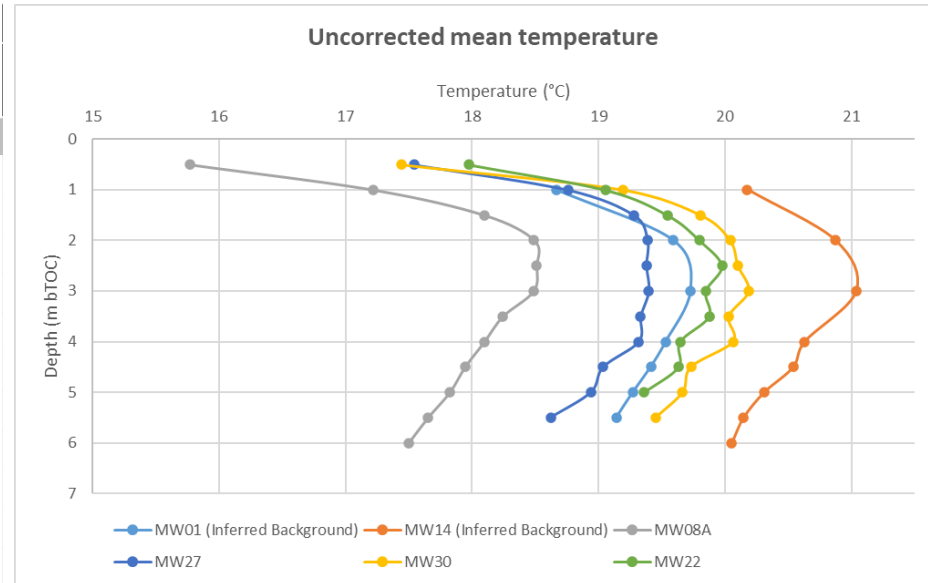
Temperature gradient (°C/m) 0.21

Lower temperature gradient

Temperature gradient (°C/m) 0.13

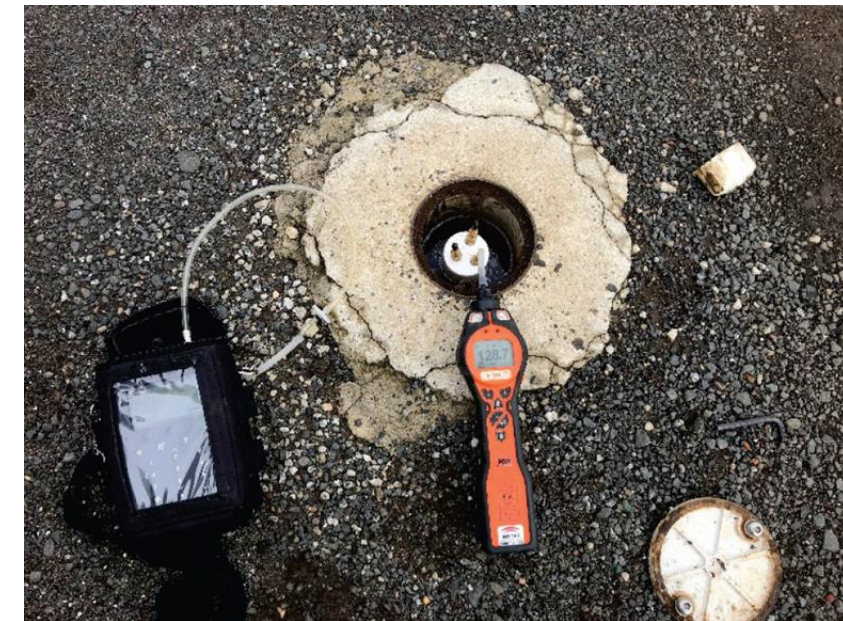
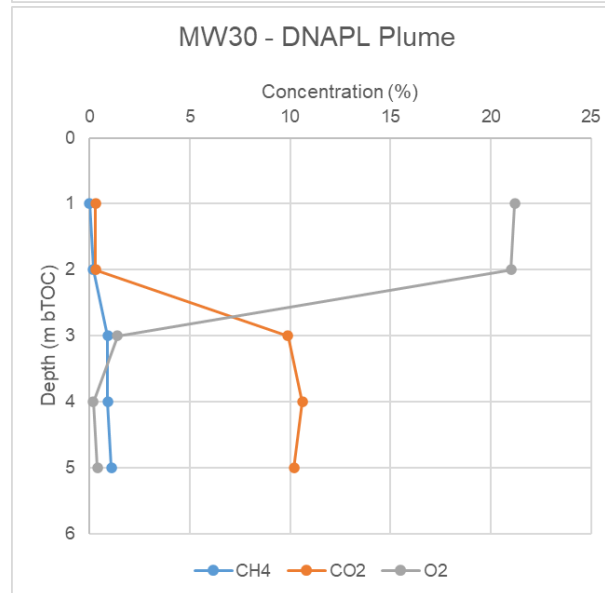
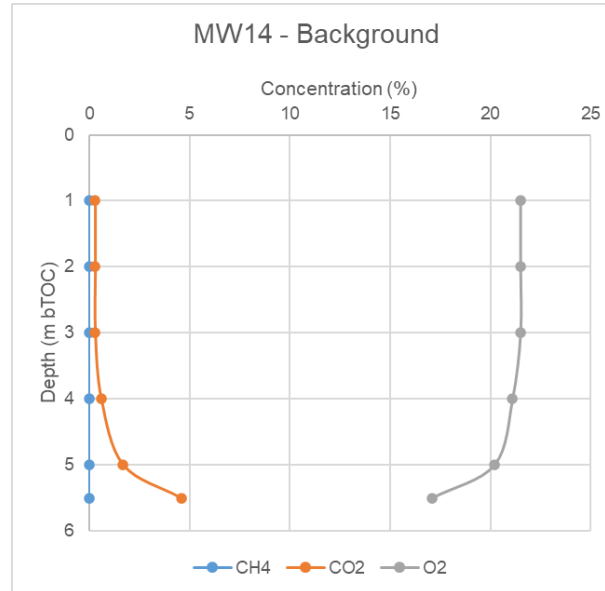
NSZD rate estimate

Assumed thermal conductivity (J/m°C/s)	1.26
Assumed heat of reaction (KJ/g)	-48
Assumed NAPL specific gravity	1.036
Temperature gradient (summation, °C/m)	0.33
Heat Flux (J/m ² /s)	0.42
NSZD rate (g/m ² /s)	0.000009
NSZD rate (kg/m ² /yr)	0.28
NSZD rate (L/m ² /yr)	0.27
NSZD rate (L/Ha/yr)	2,666



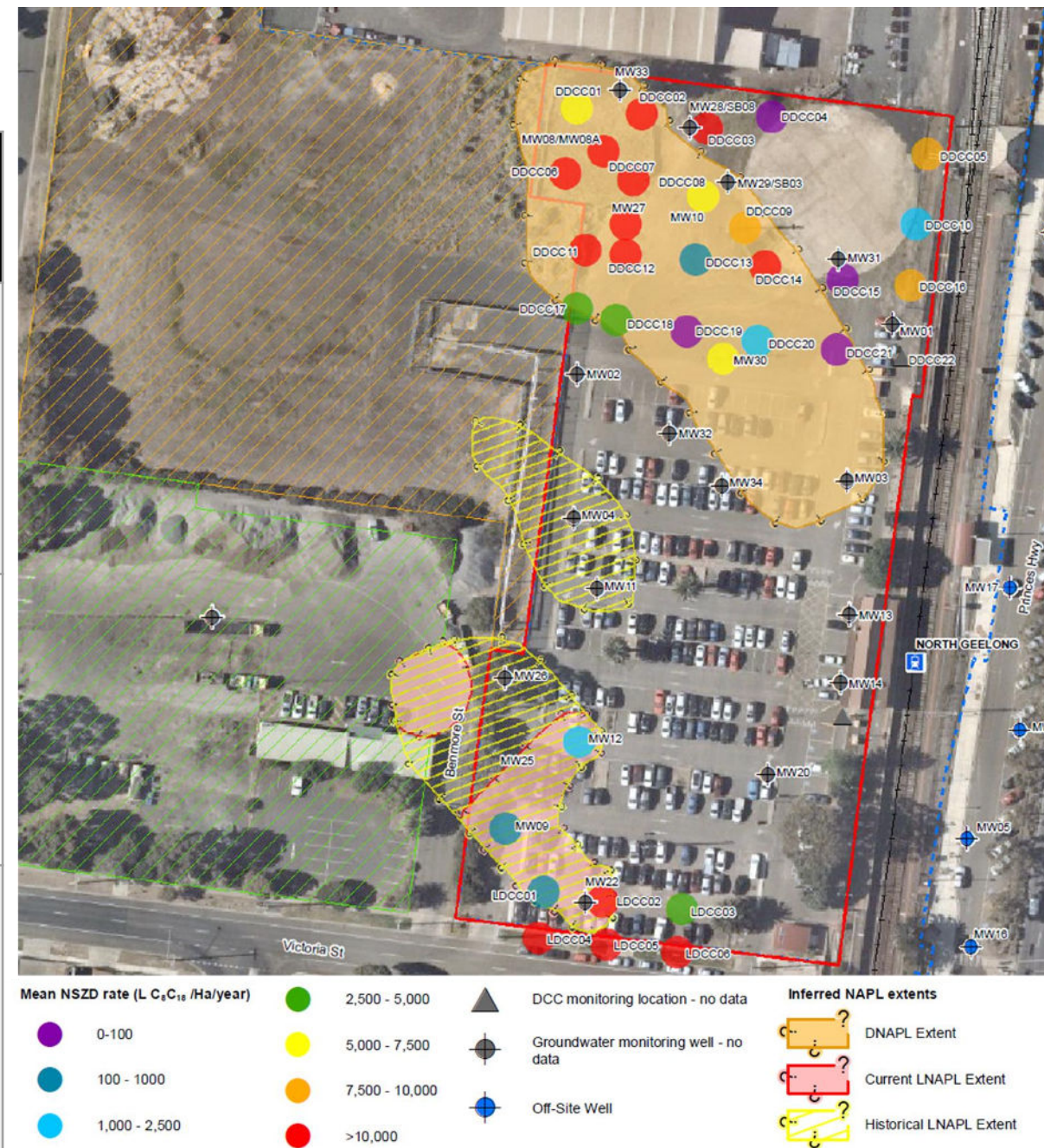
Technique 3: soil gas gradient

DNAPL Plume		
Parameter	Value	Unit
O ₂ diffusion coefficient	3.92E-07	m ² /s
O ₂ gradient calculations and background correction		
dC/dz (O ₂) at MW14	12.96	g O ₂ /m ³ m
dC/dz (O ₂) MW08A corrected	4.12	g O ₂ /m ³ m
dC/dz (O ₂) MW30 corrected	55.98	g O ₂ /m ³ m
O ₂ diffusive flux at MW08A and MW30		
O ₂ Diffusive flux at MW08A	0.13	g O ₂ /m ² day
O ₂ Diffusive flux at MW30	1.89	g O ₂ /m ² day
Stoichiometric calculations		
Molecular weight C ₈ H ₁₈	114	g/mol
Molecular weight O ₂	32	g/mol
Mass C ₈ H ₁₈	114	g
Mass O ₂	400	g
C ₈ H ₁₈ : O ₂	0.285	g C ₈ H ₁₈ /g O ₂
Conversion of O ₂ diffusive flux to NSZD rate		
NSZD rate	0.04 (MW08A) – 0.54 (MW30)	g/m ² /day
NSZD rate	140 (MW08A) – 1,902 (MW30)	L/ha/yr



Summary of results

Measurement technique	Mean NSZD rate estimate (L/ha/yr)	Mean NSZD rate estimate (L/m ² /yr)	Mean NSZD rate estimate (gal/acre/yr)
Soil gas gradient	1,000	0.1	100
CO ₂ efflux	12,500	1.2	1,300
Biogenic heat	3,000	0.3	340



Conclusions

1. NSZD monitoring techniques for LNAPL will also be applicable for certain types of DNAPL
2. NSZD rates typical for DNAPL may be less than LNAPL
3. bias in surficial CO₂ efflux methods at paved sites may be an order of magnitude or more
4. NSZD is a viable DNAPL remedial/management consideration





NSZD of DNAPL?

It's a thing.

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