NSZD of DNAPL: Is it a Thing?

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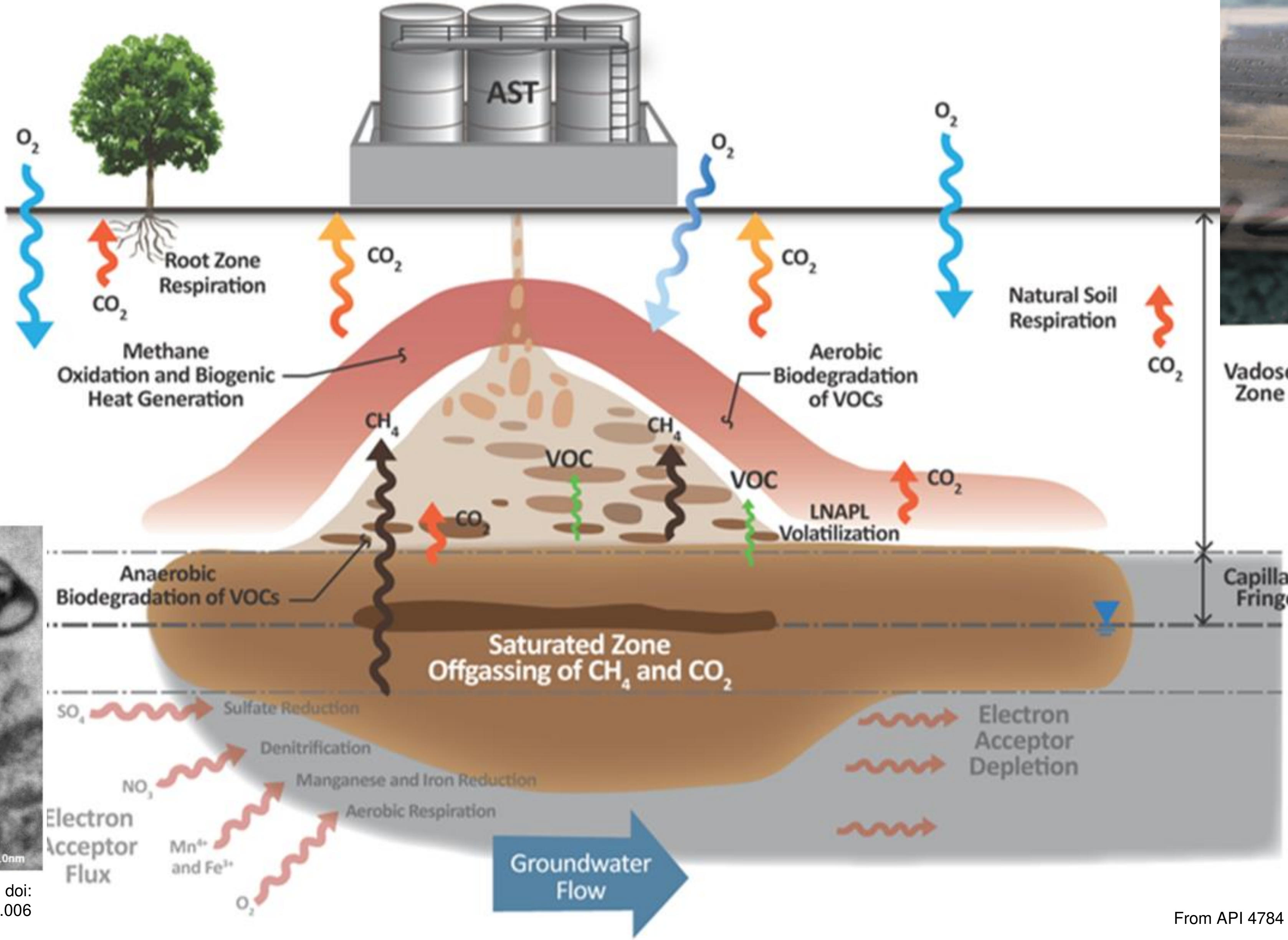
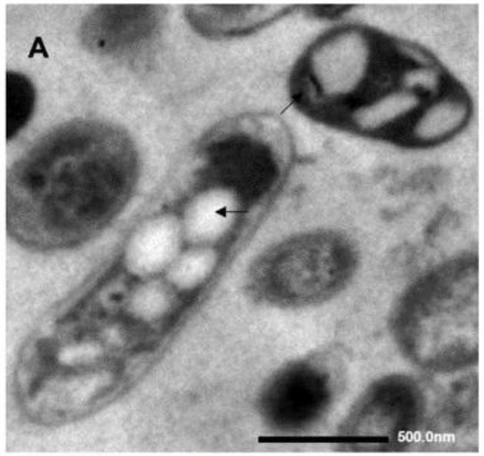
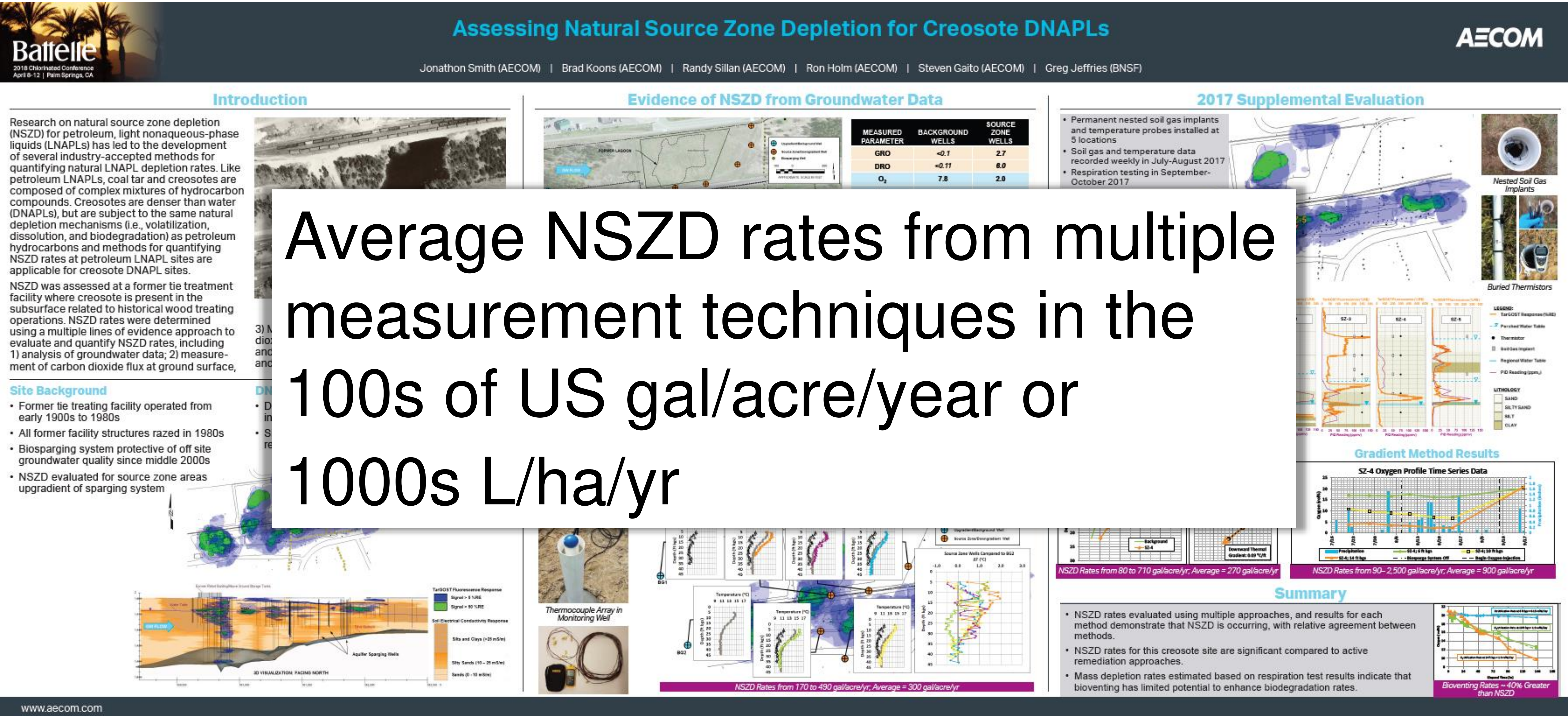
NSZD with LNAPL





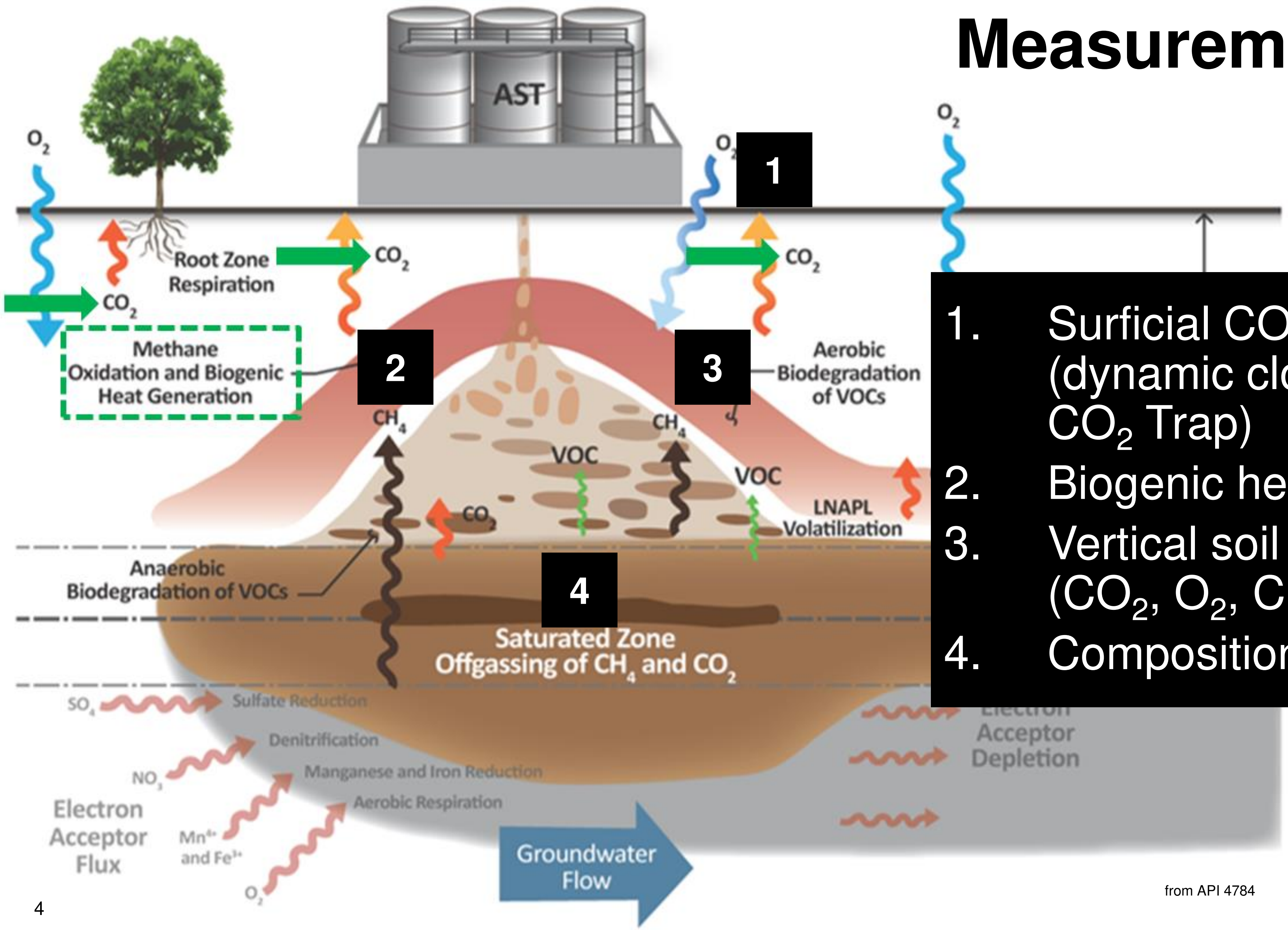
from Ng et al, 2014, doi:
10.1016/j.jconhyd.2014.04.006

From API 4784



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

Measurement options



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

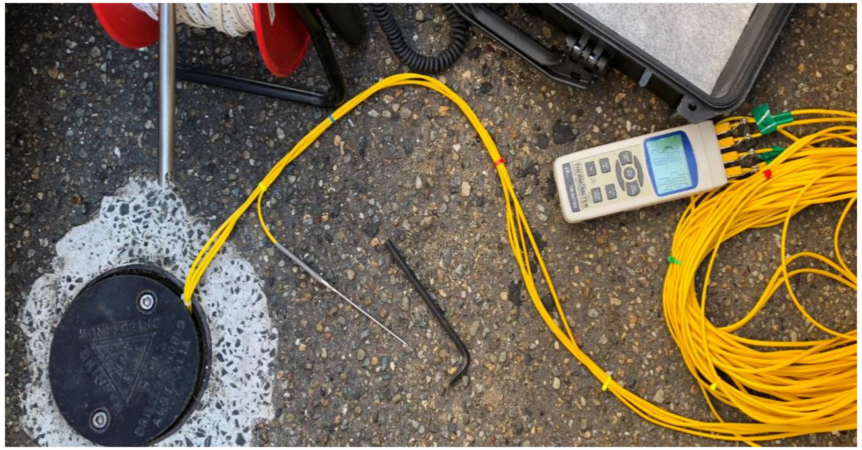
from API 4784

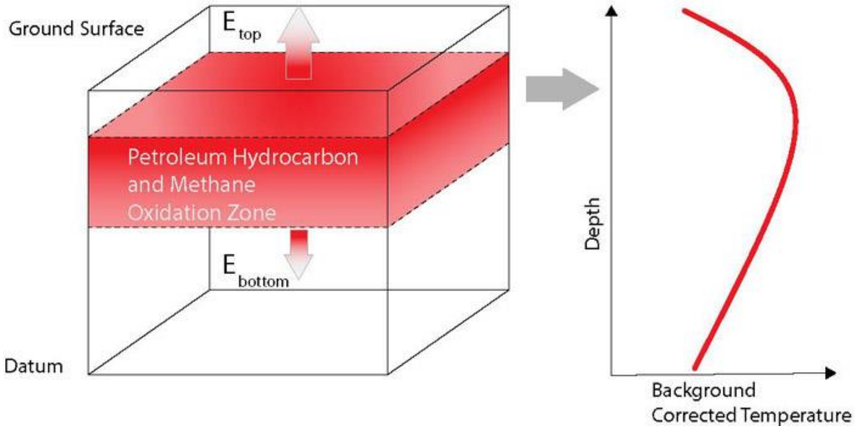
Technique 1: dynamic closed chamber

– 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., **CH_4 oxidation = 48 kJ/g $C_{10}H_{22}$**)
– Correct with background locations of modelled background profile





from ITRC LNAPL-3

Technique 3: soil gas gradient

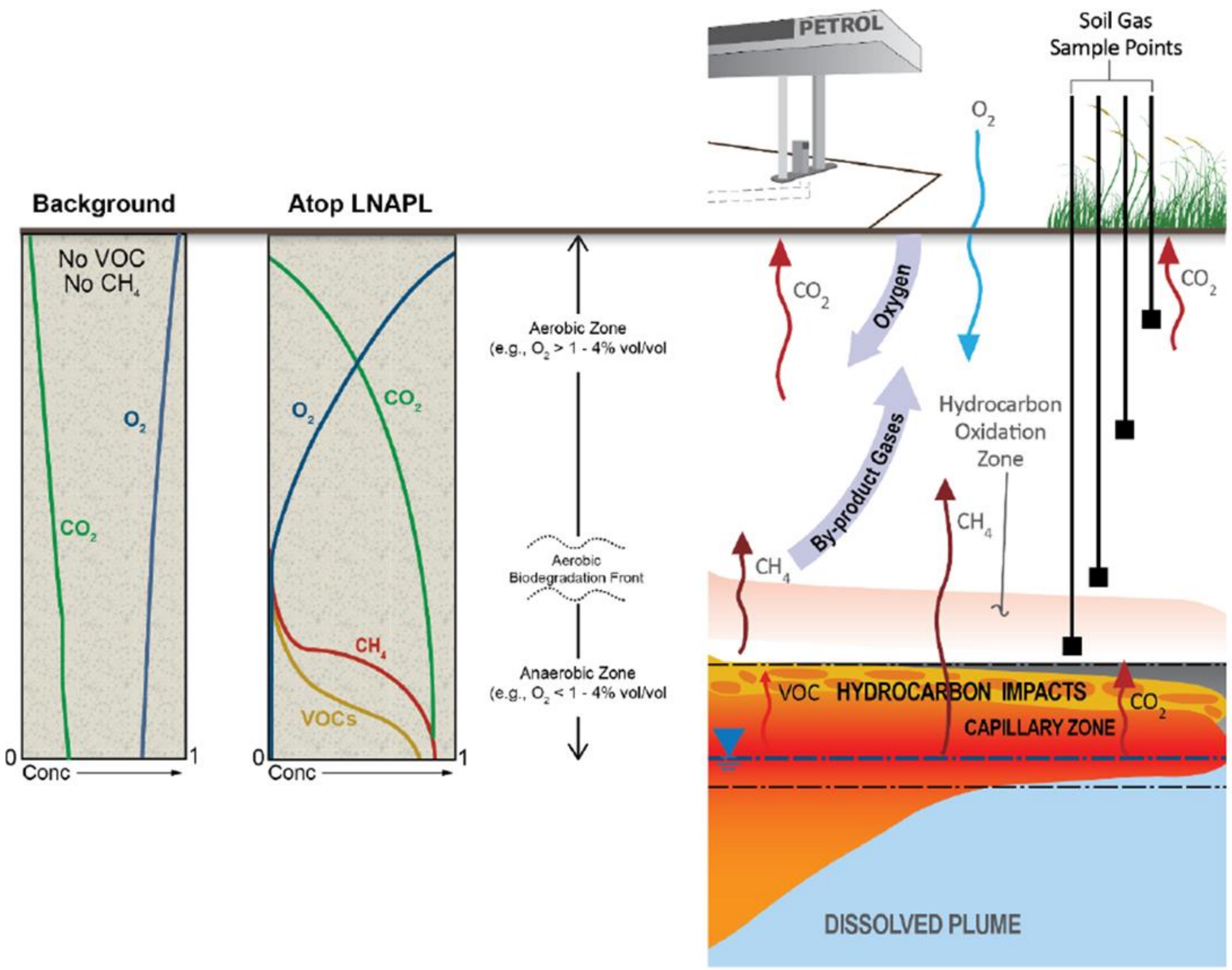
Fick's Law

[Diffusive O_2 flux, J] =

[O_2 concentration gradient] x

[diffusivity, D_v]

0.3g C_8H_8 (LNAPL)/g O_2

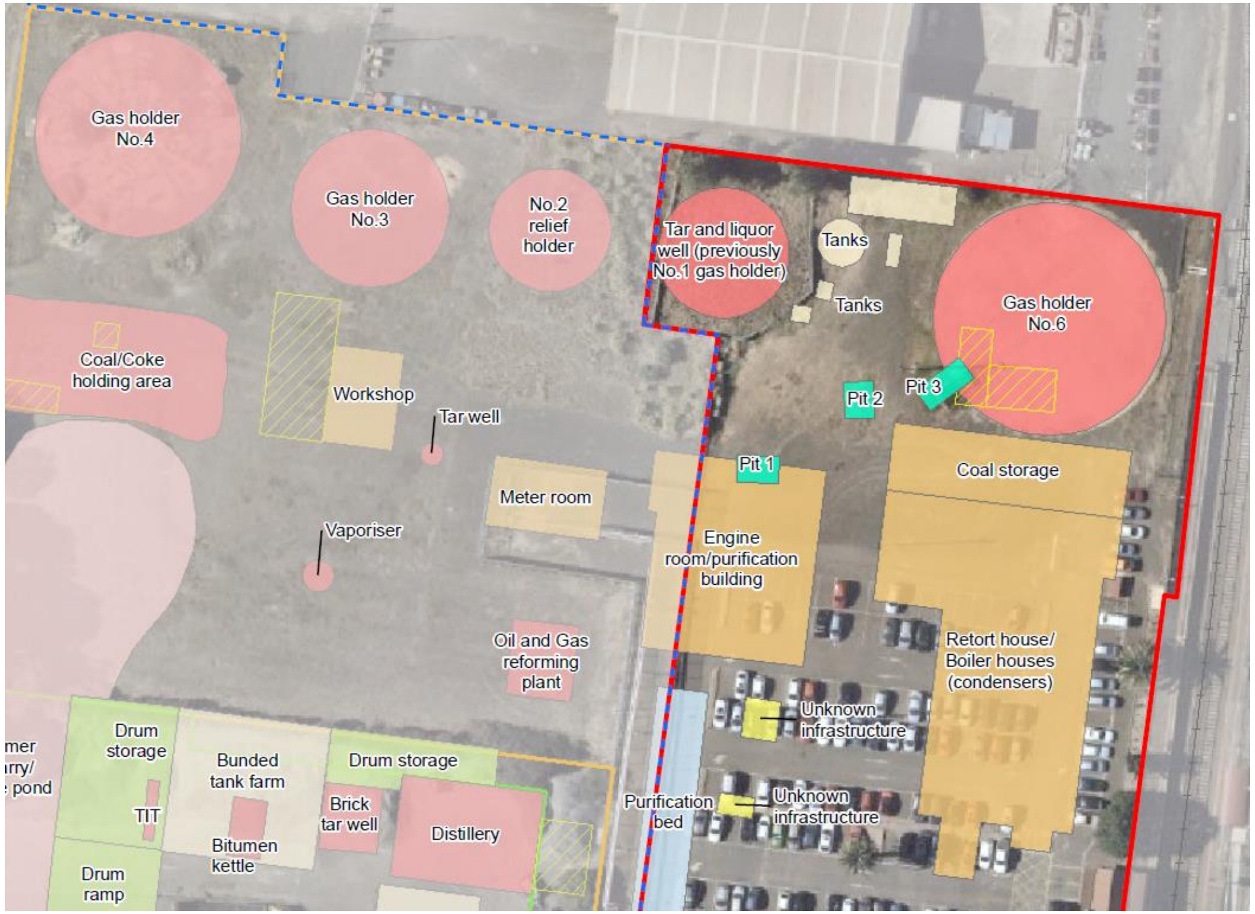


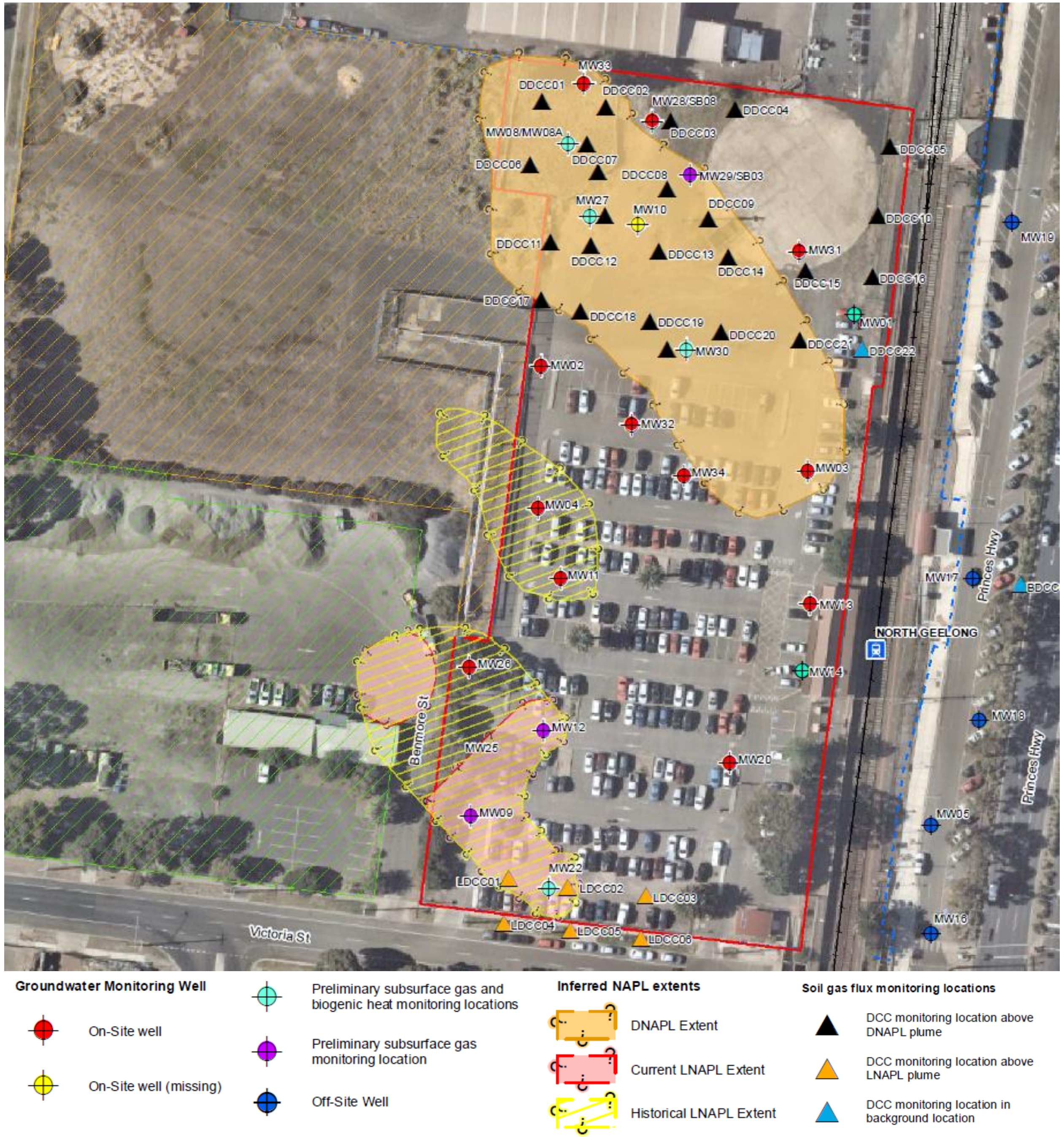
from CRC CARE Technical Report 44

The test site

- Former MGP site with coal tar DNAPL

The site – former MGP



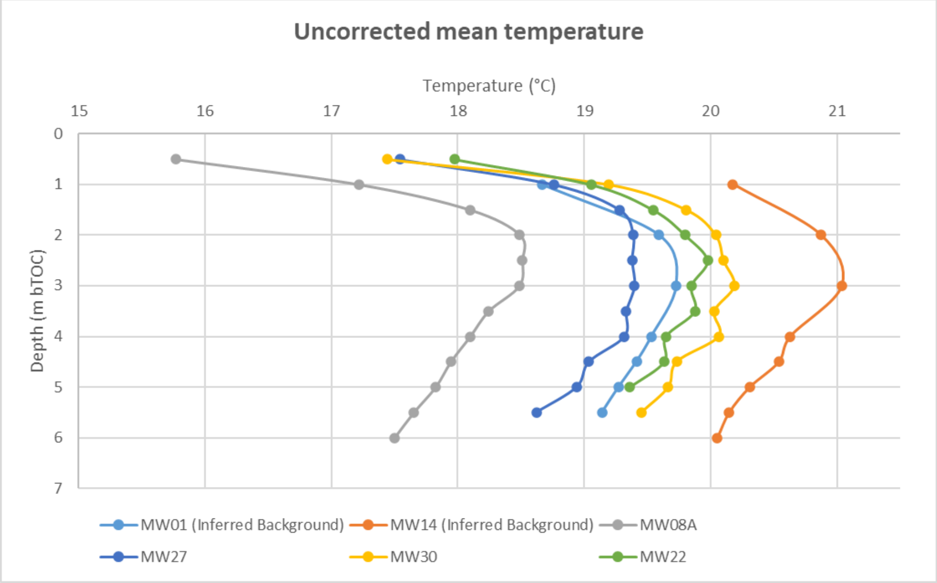


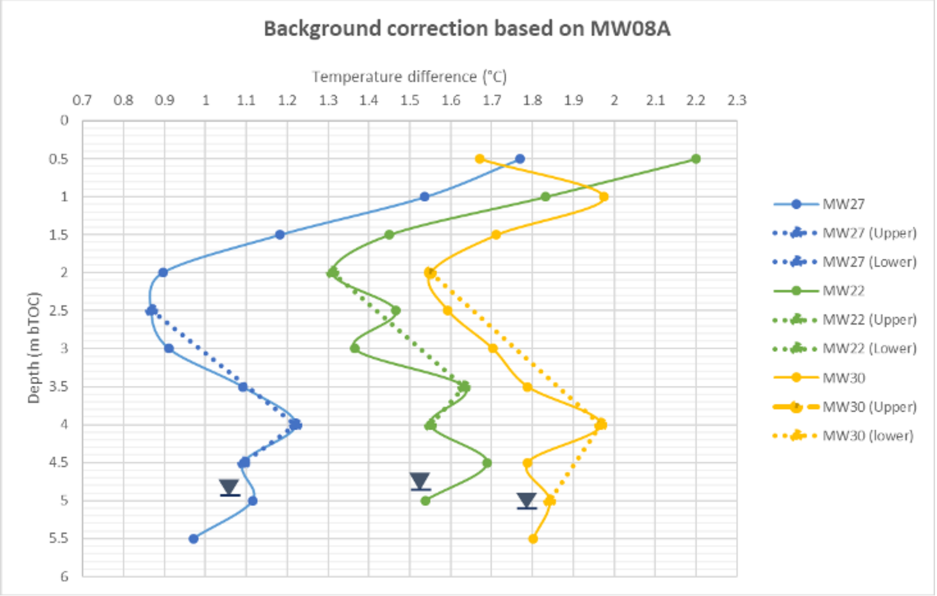
Technique 1: dynamic closed chamber

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

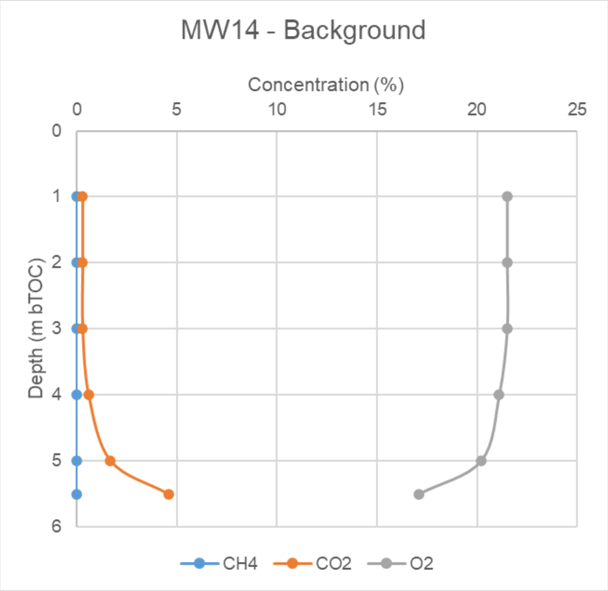
Depth (metres bgs)	MW08A (background)	MW30	
		Temperature (°C)	ΔT (°C)
Temperature profiles			
0.5	15.77344579	17.44444241	1.670996612
1	17.22183411	19.19607255	1.974238435
1.5	18.09723435	19.8090903	1.711855958
2	18.4908472	20.04104907	1.550201869
2.5	18.51010876	20.10343715	1.593328388
3	18.48524486	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**	

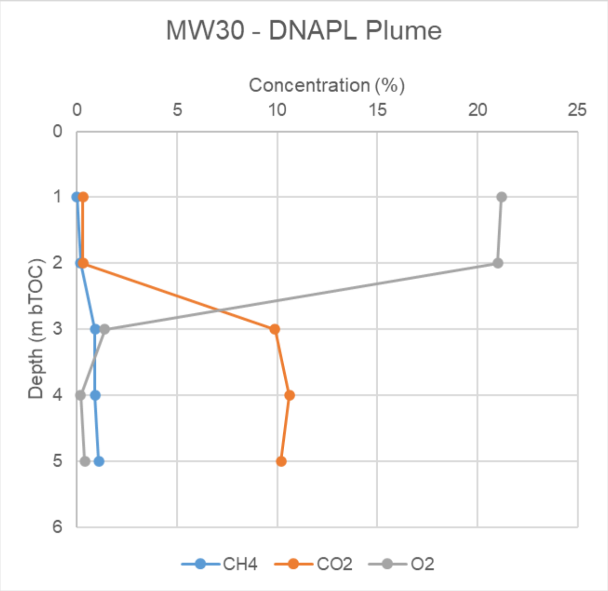


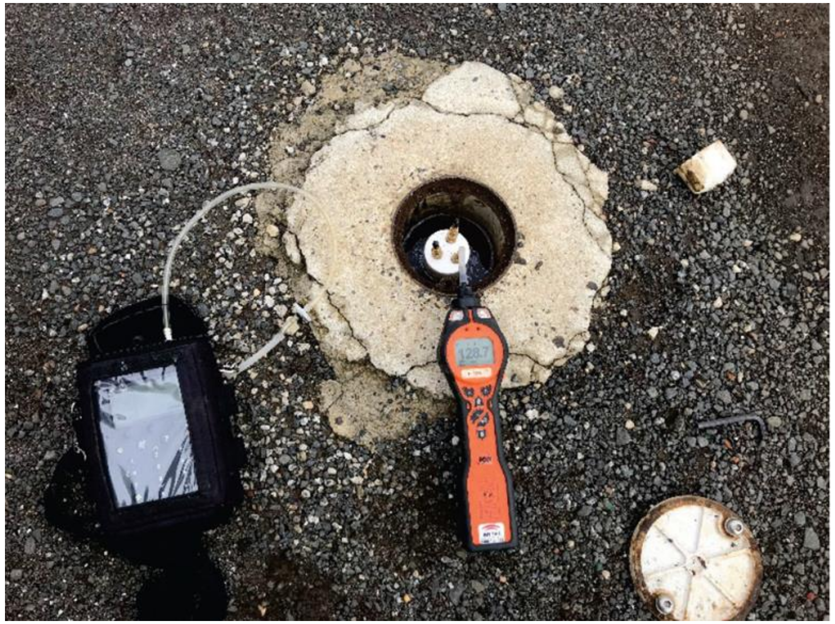


Technique 3: soil gas gradient

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^3m
dC/dz (O_2) MW08A corrected	4.12	g O_2/m^3m
dC/dz (O_2) MW30 corrected	55.98	g O_2/m^3m
O_2 diffusive flux at MW08A and MW30		
O_2 Diffusive flux at MW08A	0.13	g O_2/m^2day
O_2 Diffusive flux at MW30	1.89	g O_2/m^2day
Stoichiometric calculations		
Molecular weight C_8H_{18}	114	g/mol
Molecular weight O_2	32	g/mol
Mass C_8H_{18}	114	g
Mass O_2	400	g
C_8H_{18} : O_2	0.285	g C_8H_{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

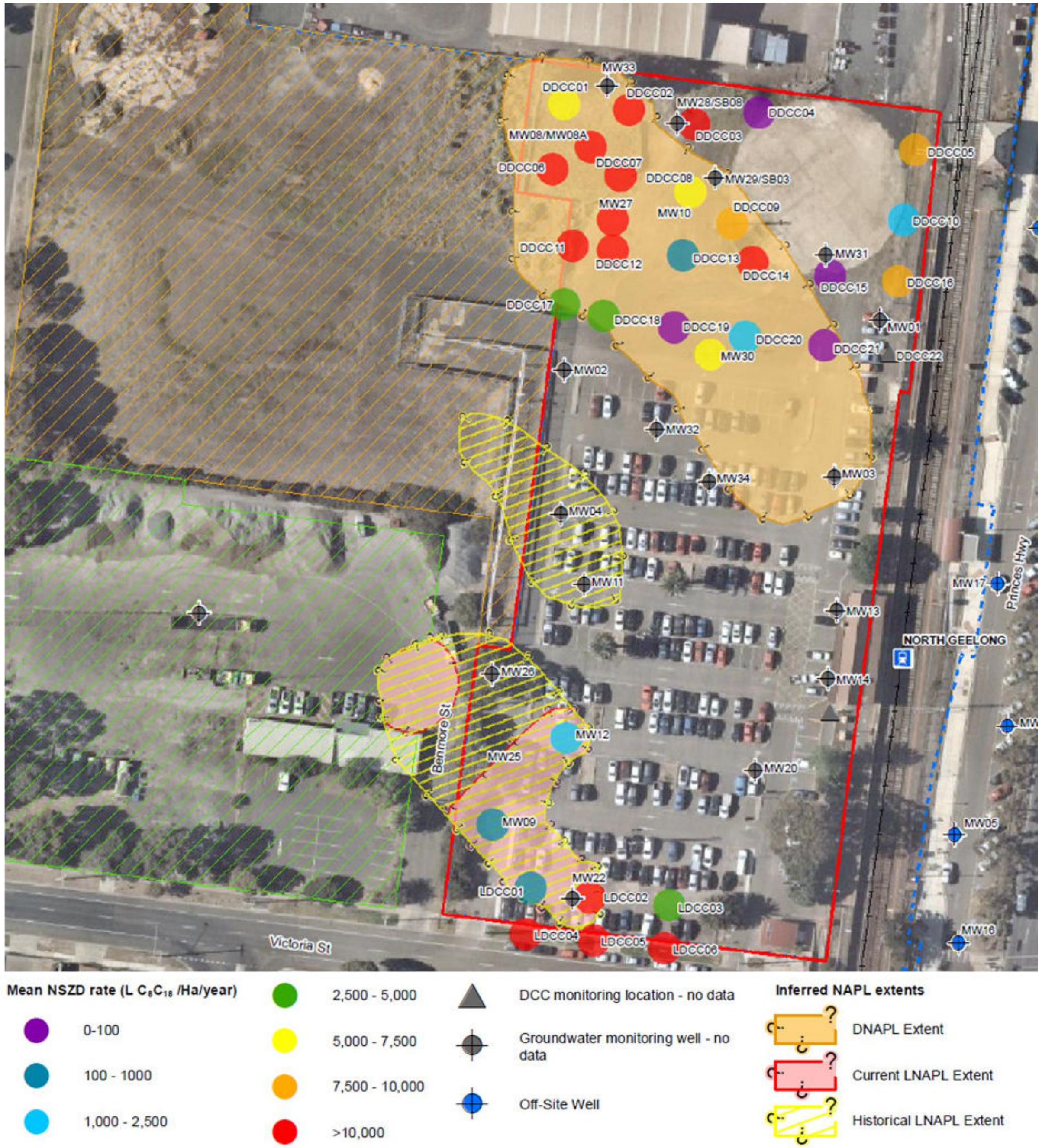






Summary of results

Measurement technique	Mean NSZD rate estimate (L/ha/yr)	Mean NSZD rate estimate (L/m²/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 CO_2 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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