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NAPL Specialist

Welcome

Evaluating NSZD

→ via the biogenic heat method at complex sites

OR…

Why doesn't my NSZD data look anything like the published data?

Agenda

- Overview of NSZD
- Common measurement methods
- Biogenic heat method
- Case study
- Discussion

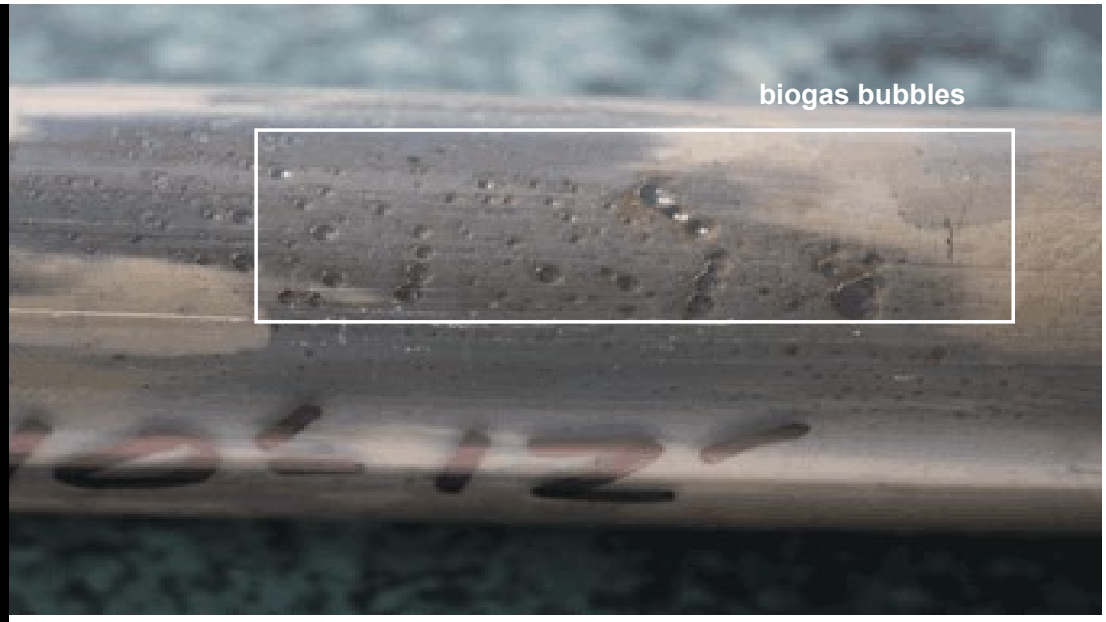
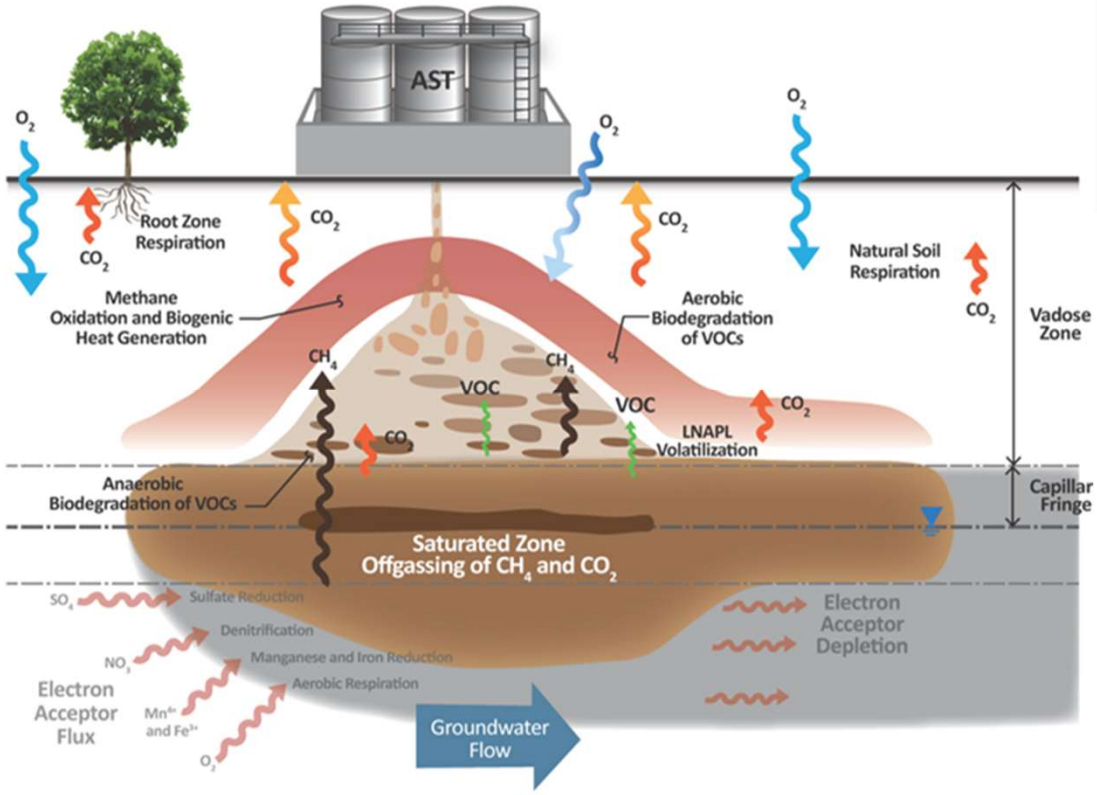


Photo courtesy of Julio Zimbron / E-Flux LLC

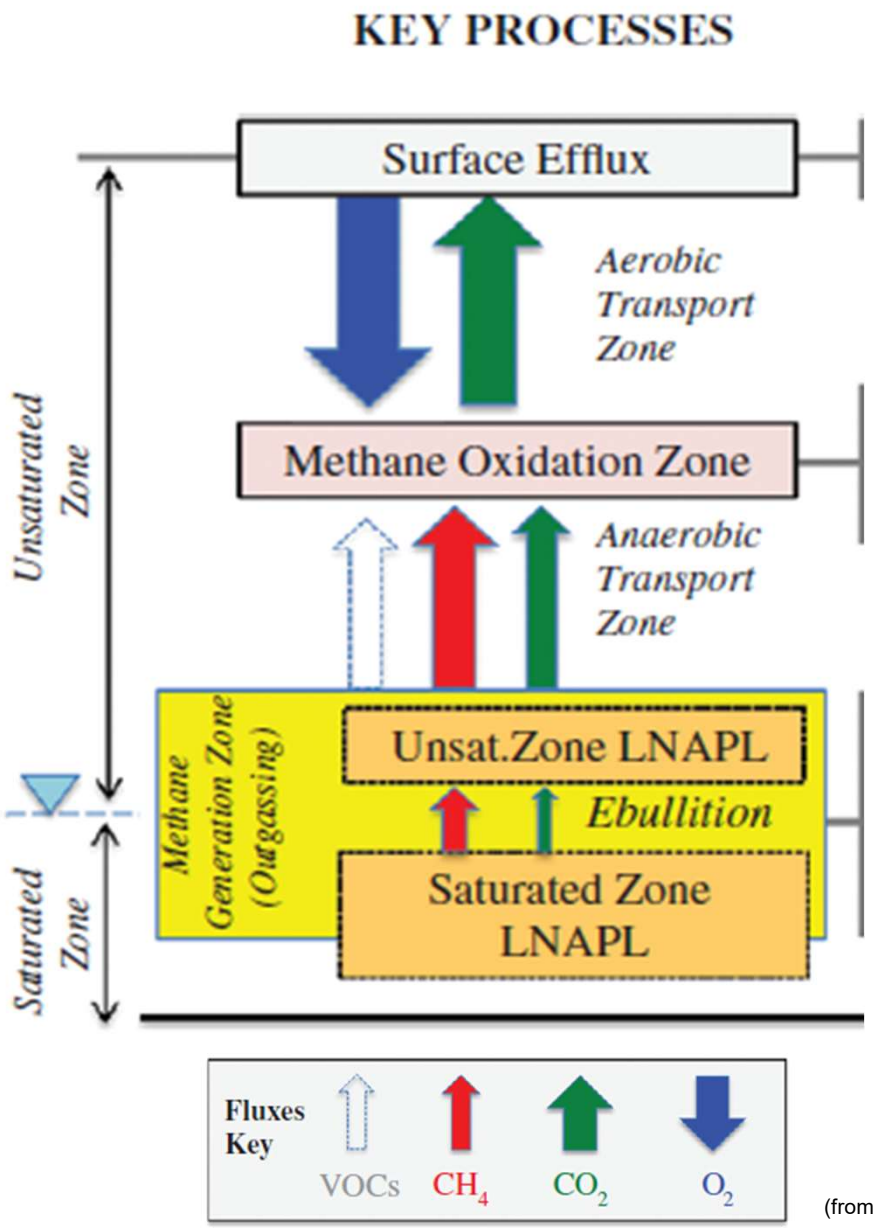
Overview of NSZD

NSZD overview



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

- Natural source zone depletion (NSZD)
- All petroleum degradation processes: dissolution, volatilization, biodegradation
- Reduces LNAPL mass in the subsurface
- Occurs throughout the LNAPL body
- Degradation of all hydrocarbons in the LNAPL
- Always occurring
- Ultimate LNAPL depletion process



(from Garg et. al, 2017)

NSZD overview

- Methanogenesis typically dominates
- Methane aerobically oxidized in the vadose zone
- The gaseous expression can be used to estimate LNAPL mass losses
- Methane oxidation exothermic reaction

Common measurement methods

Measurement methods: vapor phase

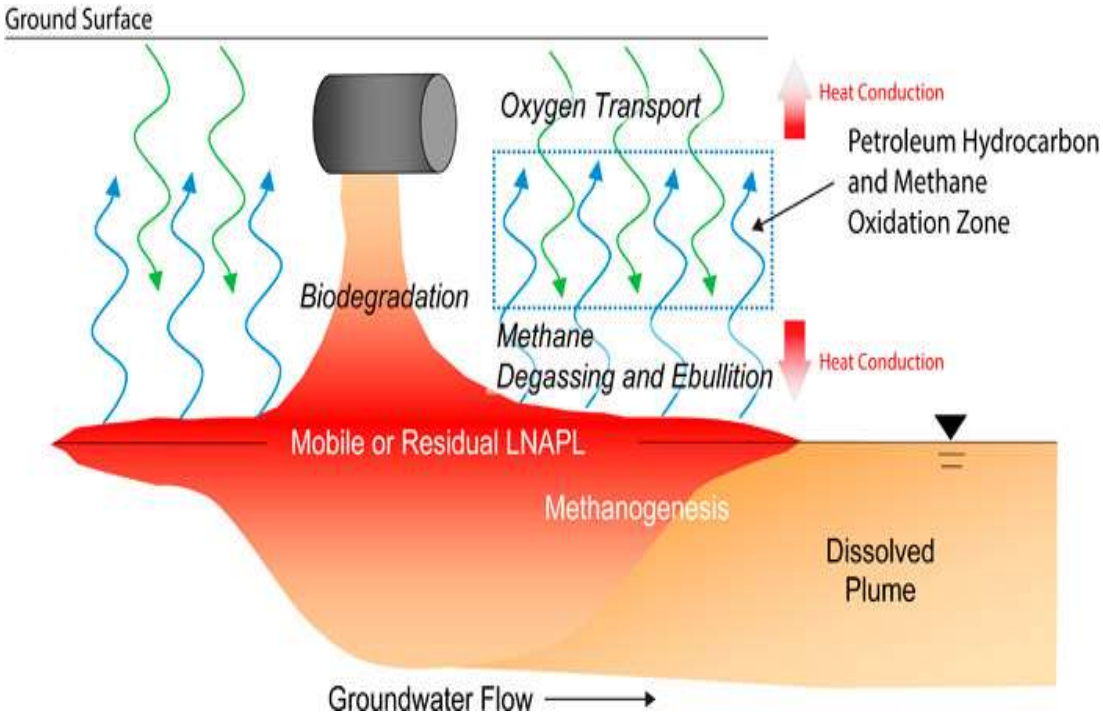
- Measurement of O_2, CH_4 and/or CO_2 gas(es)
  - Surface CO_2 efflux methods
    - Dynamic flux chamber (DCC)
    - Passive CO_2 Traps
  - Subsurface soil gases
    - Soil gas gradient method
- Conversion to LNAPL degradation rate using assumed stoichiometry
- Must correct for background

DCC Method

Passive CO_2 Flux Trap Method

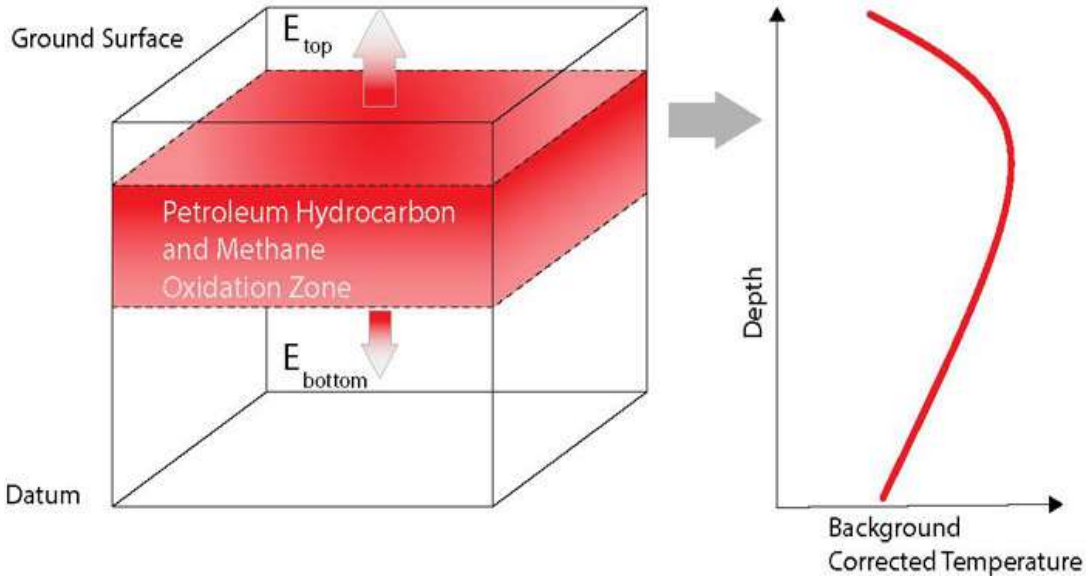
Measurement methods: temperature

- Biogenic heat method
- Methane oxidation - exothermic process
- Temperature anomalies (order of 1-2˚C)
- Background correction
- Conversion to NSZD rate using heats of reaction and assumed stoichiometry



Petroleum hydrocarbon and methane oxidation zone (from ITRC LNAPL-3, 2018)

Biogenic heat method

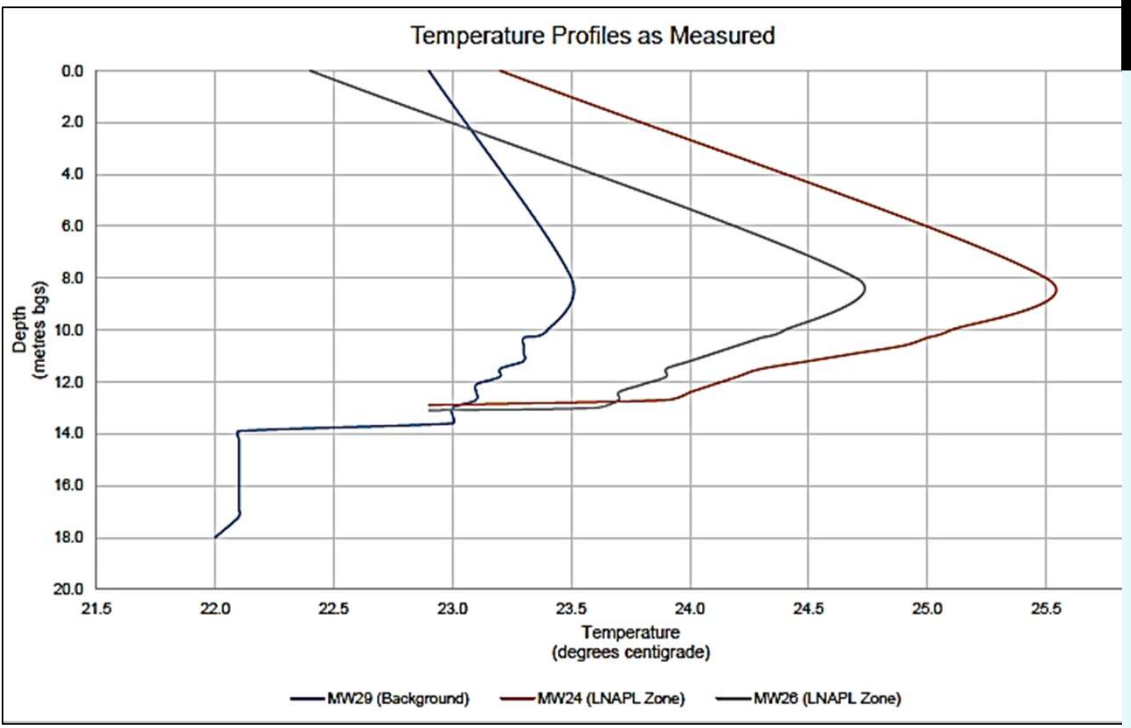


(ITRC LNAPL-3, 2018)

Biogenic heat method

- Determine subsurface temperature profiles
- Multiple depths through methane-oxidation zone
- Existing wells or dedicated installations
- Short-term snapshot data (thermocouple)
- Longer-term average (temperature loggers)
- Background correction

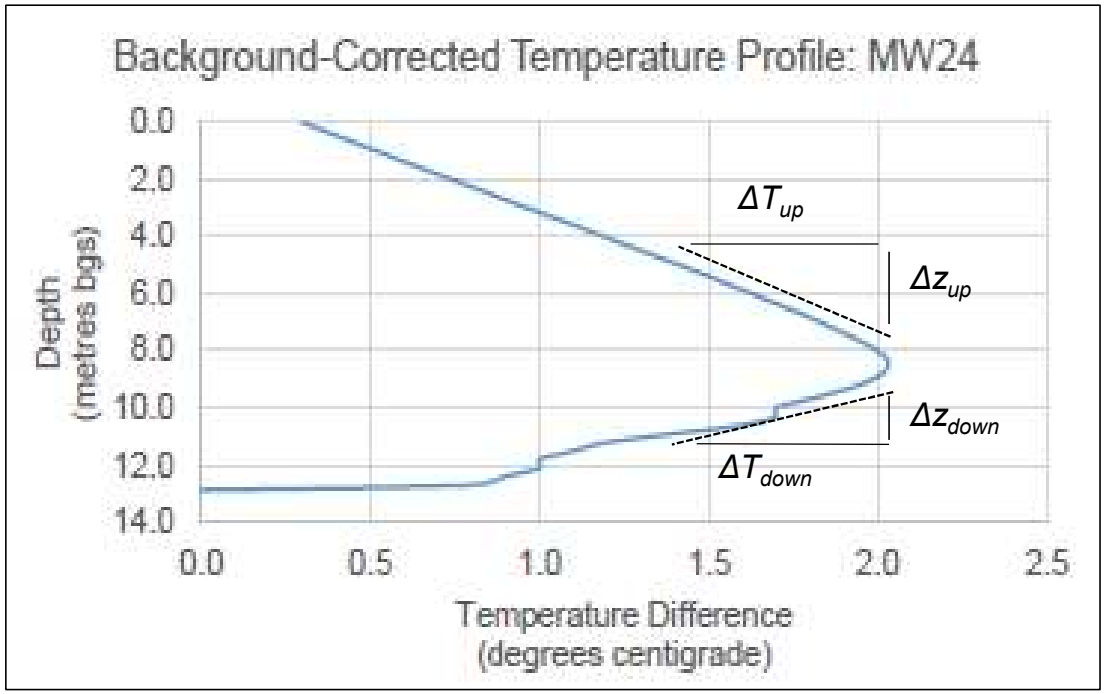
Biogenic heat method



(from CRC-CARE Tech Report 44)

- From CRC-CARE Technical Report 44
  - Data collection and NSZD rate calculations
- As measured temperature profiles (uncorrected)
- Background well (blue)
- Two LNAPL zone wells (black and red)

Biogenic heat method



(from CRC-CARE Tech Report 44)

NSZD rate determination

- Determine temperature gradients (up & down)

$$(\Delta T/\Delta z)_{upward} + (\Delta T/\Delta z)_{downward}$$

- Heat flux = (thermal conductivity of soil/rock) x (temperature gradient)

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

- NSZD rate = (heat flux) / (heat of reaction)

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

$$where\ \Delta H_{rxn} = \text{-48 kJ per gram of hydrocarbon}$$

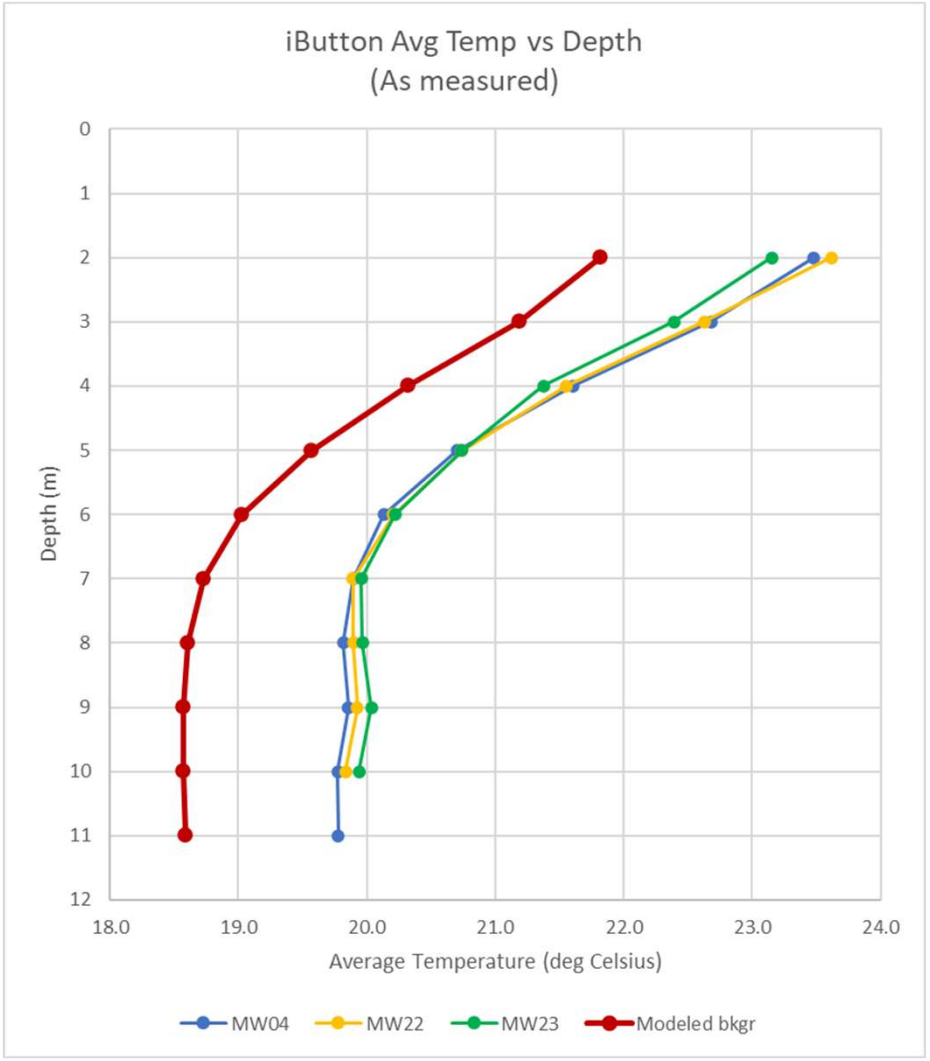
(from Sweeney & Ririe 2014)

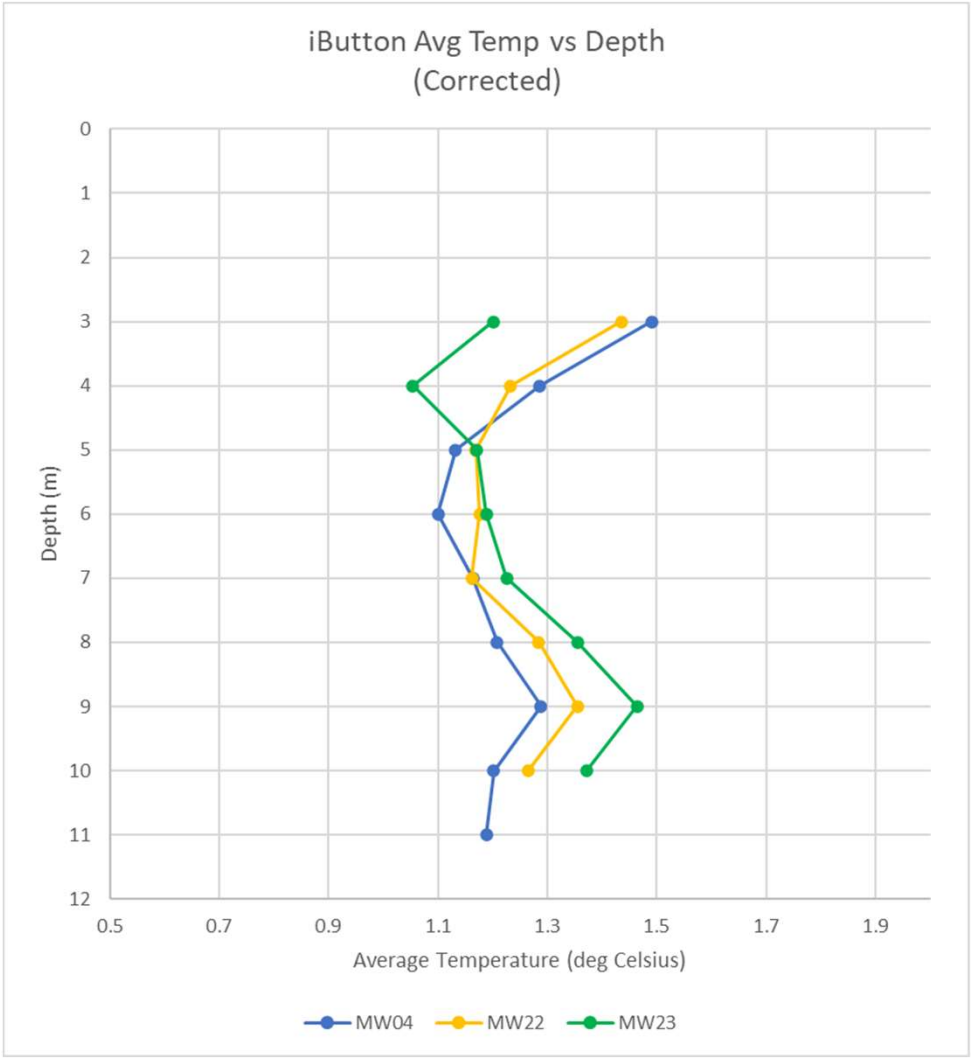
Case study

Case Study: Site History

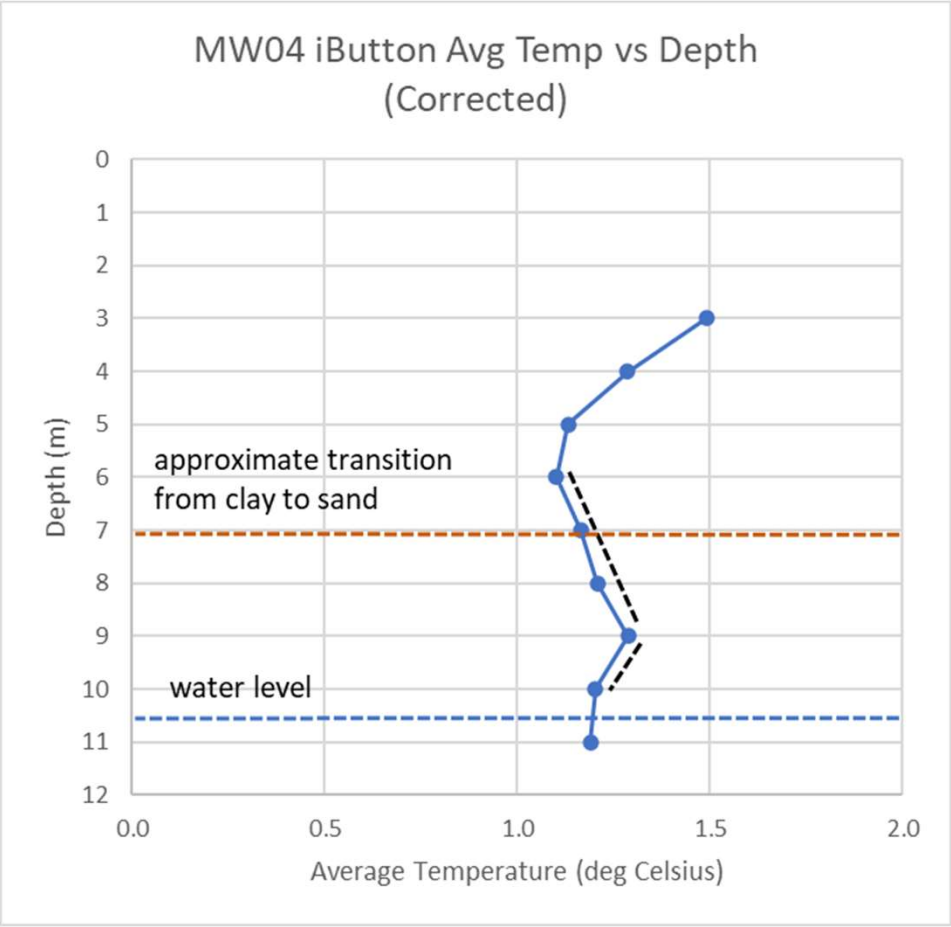
- Australian site
- Former bulk fuel depot
- Historic releases – above and below ground piping
- Impermeable ground cover
- Typical soils: clay, sandy clay, sand

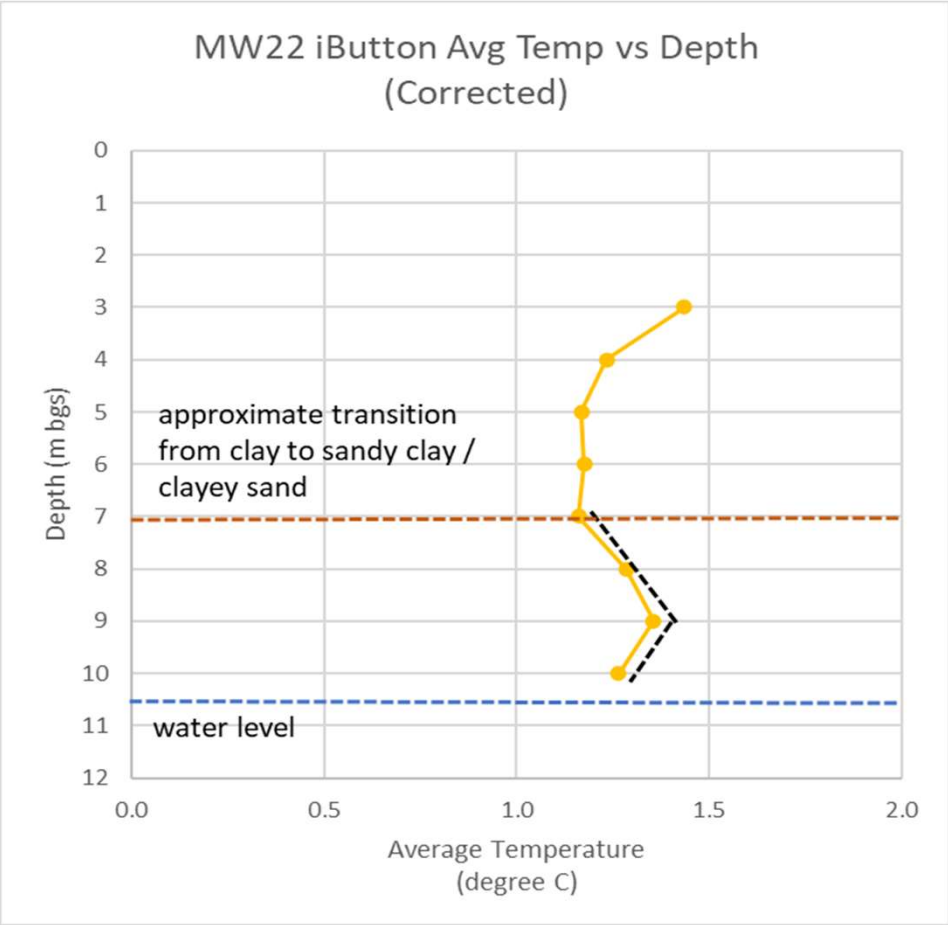
Case Study


iButton Avg Temp vs Depth
(As measured)
Depth (m)
0
1
2
3
4
5
6
7
8
9
10
11
12
18.0
19.0
20.0
21.0
22.0
23.0
24.0
Average Temperature (deg Celsius)
MW04
MW22
MW23
Modeled bkgr

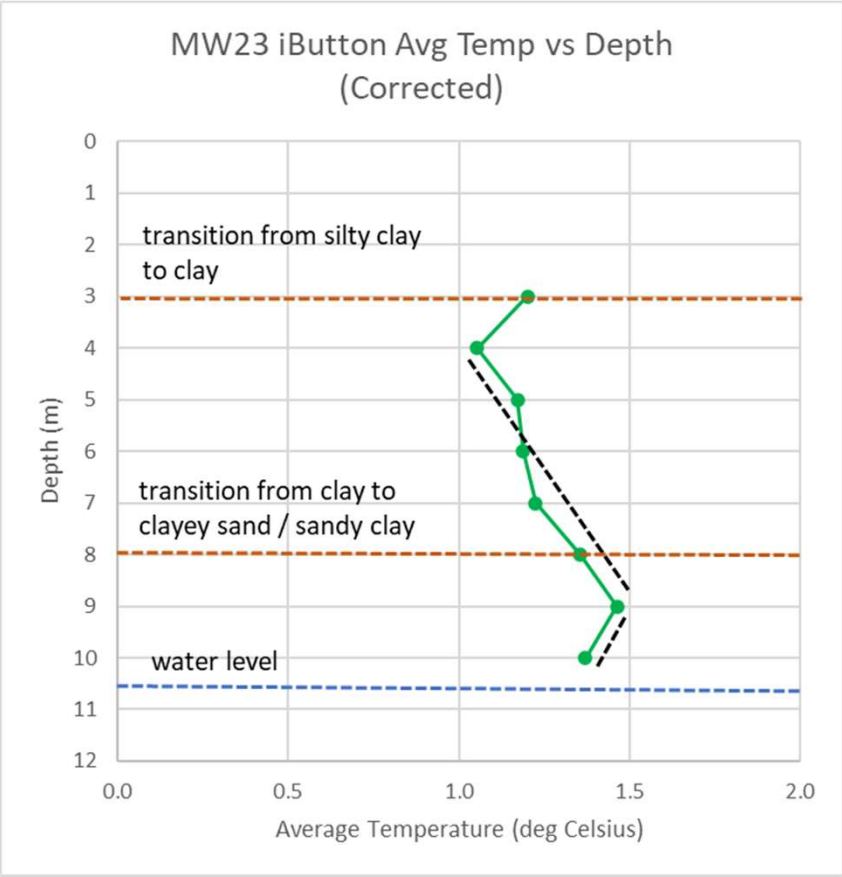

iButton Avg Temp vs Depth
(Corrected)
Depth (m)
0
1
2
3
4
5
6
7
8
9
10
11
12
0.5
0.7
0.9
1.1
1.3
1.5
1.7
1.9
Average Temperature (deg Celsius)
MW04
MW22
MW23

Case Study


MW04 iButton Avg Temp vs Depth
(Corrected)
Depth (m)
0
1
2
3
4
5
6
7
8
9
10
11
12
approximate transition
from clay to sand
water level
0.0
0.5
1.0
1.5
2.0
Average Temperature (deg Celsius)


MW22 iButton Avg Temp vs Depth
(Corrected)
Depth (m bgs)
0
1
2
3
4
5
6
7
8
9
10
11
12
approximate transition
from clay to sandy clay /
clayey sand
water level
0.0
0.5
1.0
1.5
2.0
Average Temperature
(degree C)

Case Study



Location	Temp gradient dT/dz			Heat Flux q	NSZD Rate	NSZD Rate	NSZD Rate
	(C/m)		(C/m)	(J/m2/s)	(g/m2/s)	(L/m2/yr)	(U.S. gal/ acre/yr)
	Up	**Down**	**Total**				
MW04	0.06	0.05	0.11	0.16	0.0000034	0.143	**153**
MW08	0.24	0.32	0.56	0.78	0.0000167	0.713	762
MW21	0.09	0.00	0.09	0.12	0.0000027	0.113	121
MW22	0.10	0.09	0.19	0.26	0.0000056	0.238	**254**
MW23	0.08	0.09	0.18	0.25	0.0000053	0.224	**240**
MW26	0.09	0.02	0.11	0.15	0.0000033	0.139	149
				Average NSZD Rate:		**0.262**	**280**

Discussion

Discussion

- NSZD processes have been identified at sites with fine-grained soils using the biogenic heat method.
- It may be necessary to use soil logs to interpret the temperature profiles.
- It's anticipated that only using the temperature anomaly in a limited portion of the well is a more conservative approach to determining the NSZD rate.
- We are continuing to analyze thermocouple and temperature logger data at complex sites and welcome discussion of others' successes and lessons learned.

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* Thank You

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