



# NSZD at Paved Fuel Retail Site

Remediation Technologies Symposium 2021

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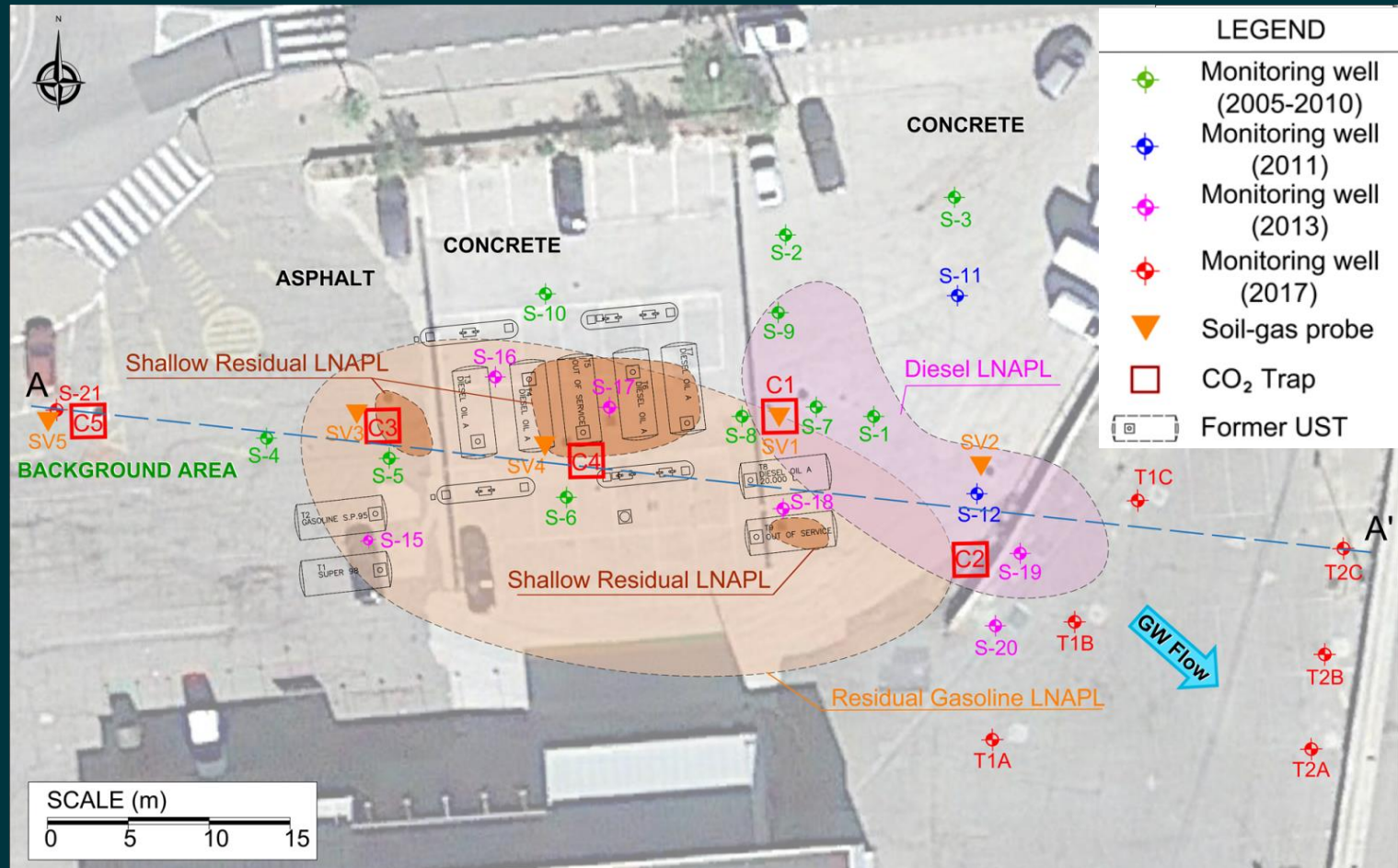
# Site Description

- Former urban retail fuelling station (1966-2009)
- 9 USTs and above-ground structures decommissioned or removed in 2009
- Surface capped with asphalt and concrete.
- Water Table at 8 to 12 m bgs
- Residual gasoline impacts in western and central portion
- Diesel LNAPL accumulations in wells to east
- Shallow residual LNAPL ( $\leq 3$  m bgs) near former USTs and dispensers



# Objectives

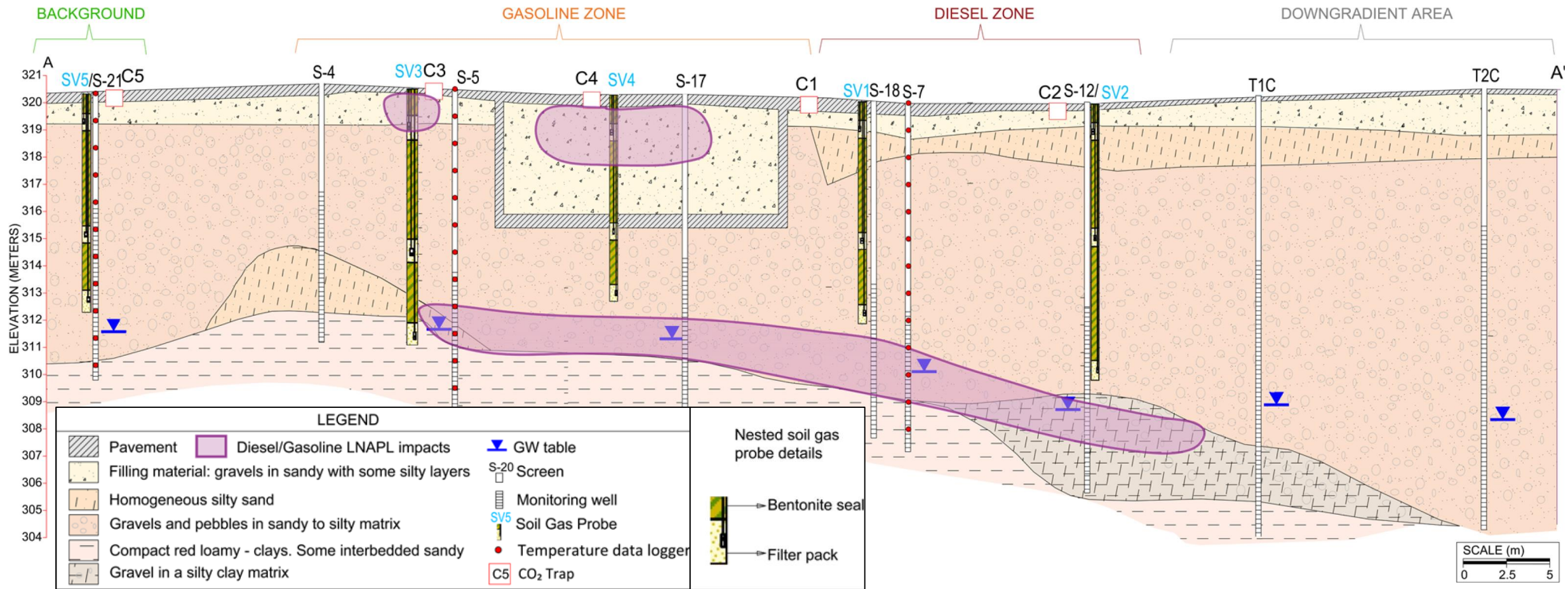
- Evaluate common NSZD methods under typical fuel retail site conditions
- Influence of capped surface on measurements and interpretation
- Compare soil gas measurements from multi-depth vapor probes and monitoring wells.



# Data Acquisition/Methodology

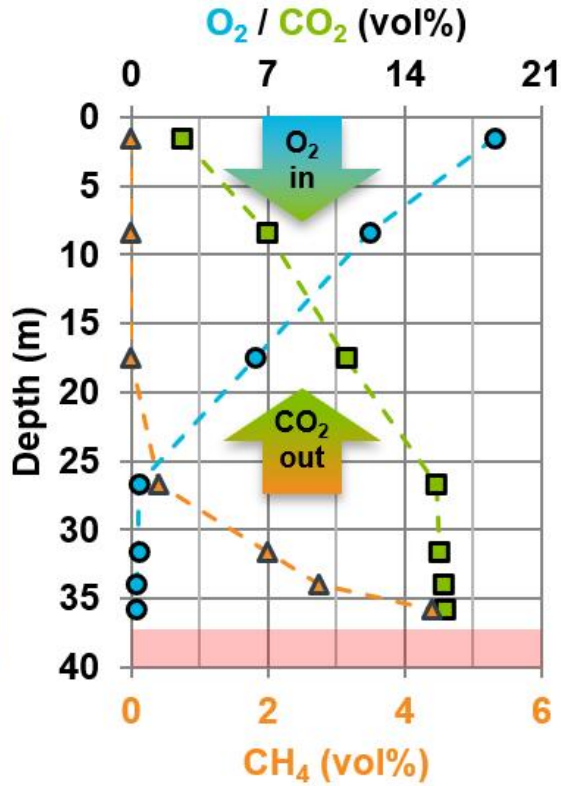
- Carbon Dioxide Traps (two events)
- Temperature profiling in wells using manual and continuous automated data collection

- Soil gas composition measured in soil gas probes and from monitoring wells screened into the unsaturated zone using low-purge methods (Sweeney and Ririe, 2017)



# NSZD Conceptual Model

## Simple Model

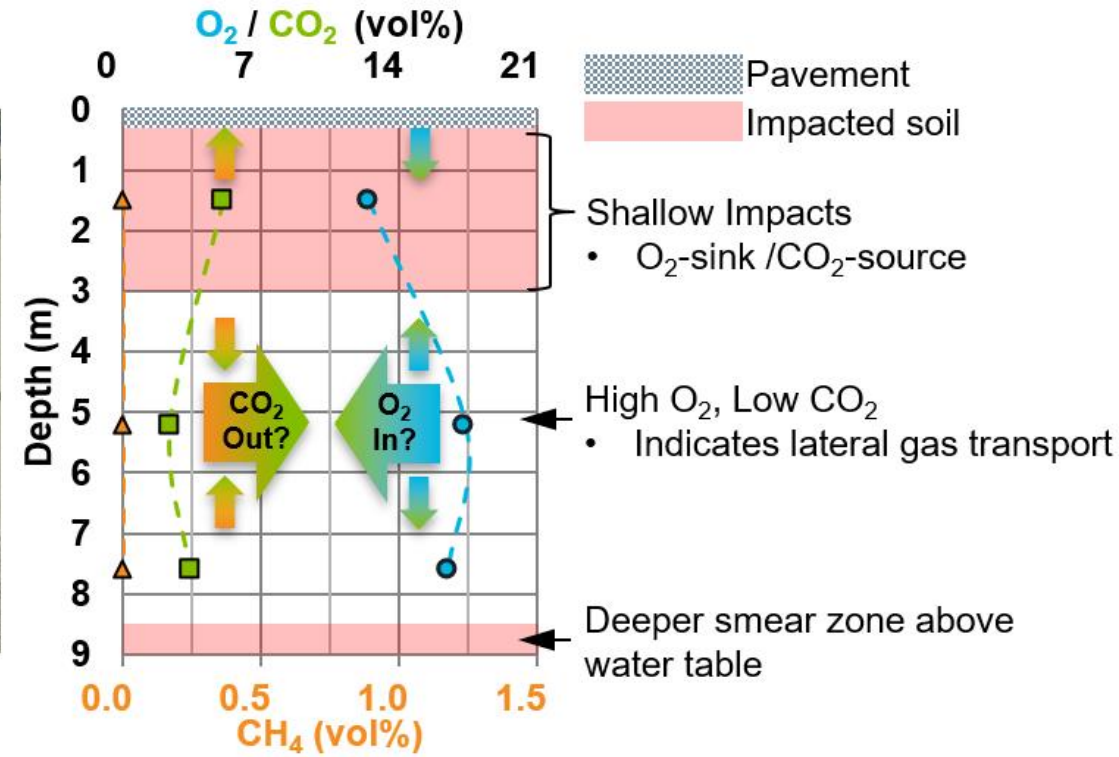


Free gas exchange between atmosphere and subsurface

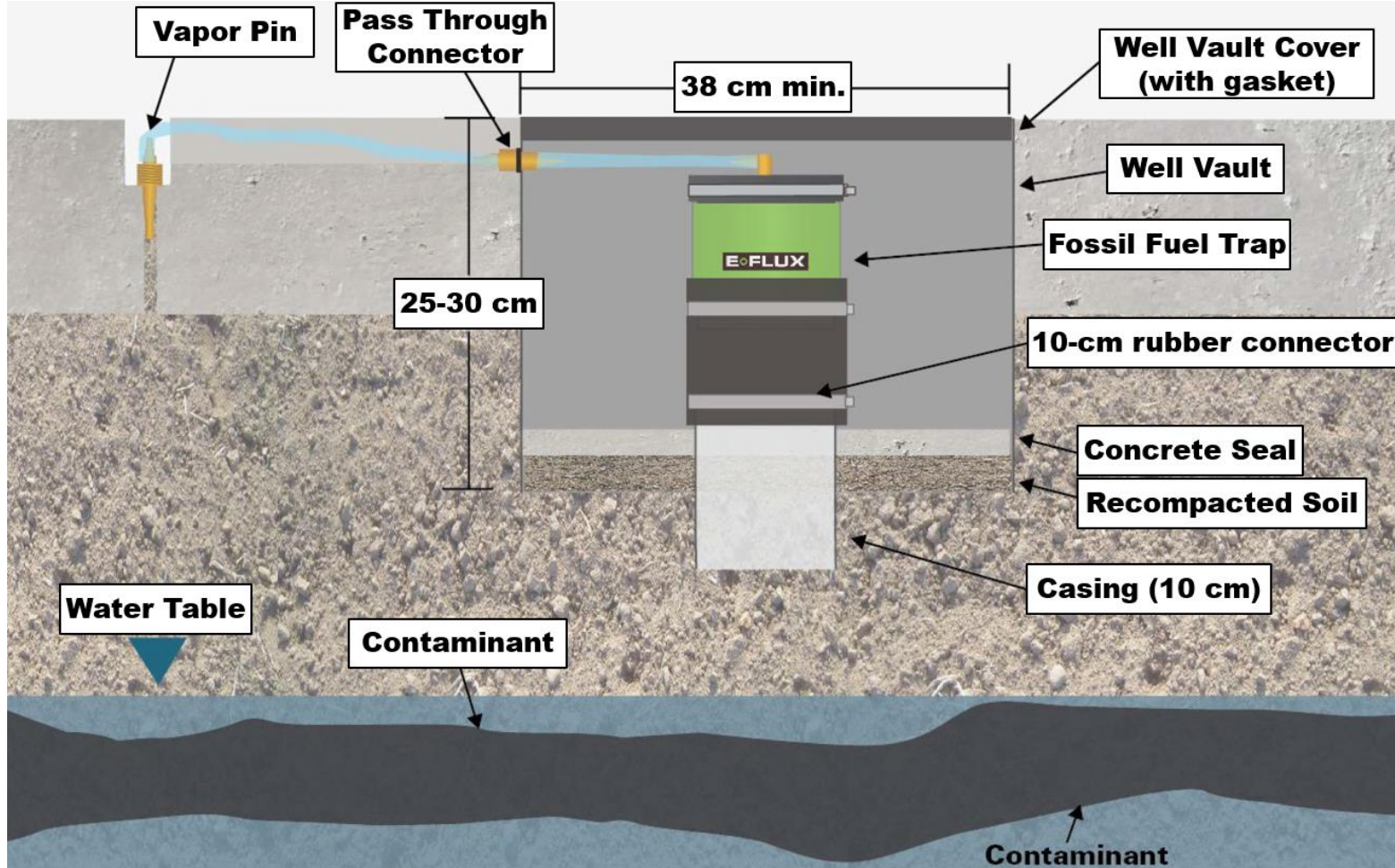


Low diffusivity layer at surface; gas exchange through cracks

## Study Site Conditions



# CO<sub>2</sub> Trap Design



# CO<sub>2</sub> Trap Results – Two Events

Trap ID: C3 (Gasoline Area)			
Date	CO <sub>2</sub> Flux (μmol /m <sup>2</sup> /s)	<sup>14</sup> CO <sub>2</sub> (pMC)	Depletion Rate (L/ha/yr)
Oct-2017	18	28	76,000
Apr-2018	4.4	35	17,000

Trap ID: C4 (Gasoline Area)			
Date	CO <sub>2</sub> Flux (μmol /m <sup>2</sup> /s)	<sup>14</sup> CO <sub>2</sub> (pMC)	Depletion Rate (L/ha/yr)
Oct-2017	26	18	130,000
Apr-2018	3.5	16	17,000

Trap ID: C1 (Diesel Area)			
Date	CO <sub>2</sub> Flux (μmol /m <sup>2</sup> /s)	<sup>14</sup> CO <sub>2</sub> (pMC)	Depletion Rate (L/ha/yr)
Oct-2017	0.29	62	690
Apr-2018	0.38	98	150

Trap ID: C2 (Diesel Area)			
Date	CO <sub>2</sub> Flux (μmol /m <sup>2</sup> /s)	<sup>14</sup> CO <sub>2</sub> (pMC)	Depletion Rate (L/ha/yr)
Oct-2017	0.76	81	1,000
Apr-2018	<Blank	89	0

Trap ID: C5 (Background)			
Date	CO <sub>2</sub> Flux (μmol /m <sup>2</sup> /s)	<sup>14</sup> CO <sub>2</sub> (pMC)	Depletion Rate (L/ha/yr)
Oct-2017	8.5	66	19,000
Apr-2018	2.2	62	5,300

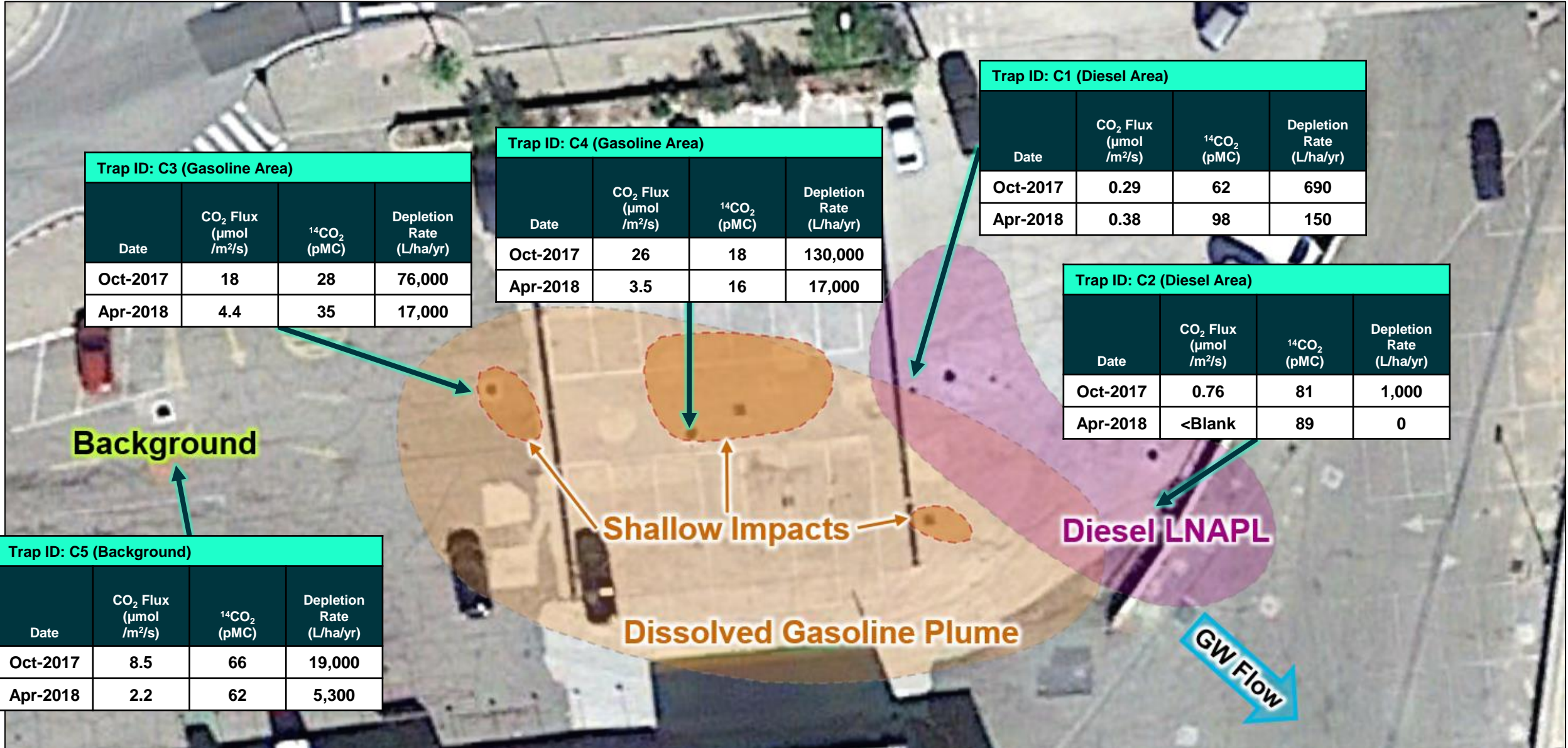
Background

Shallow Impacts

Dissolved Gasoline Plume

Diesel LNAPL

GW Flow



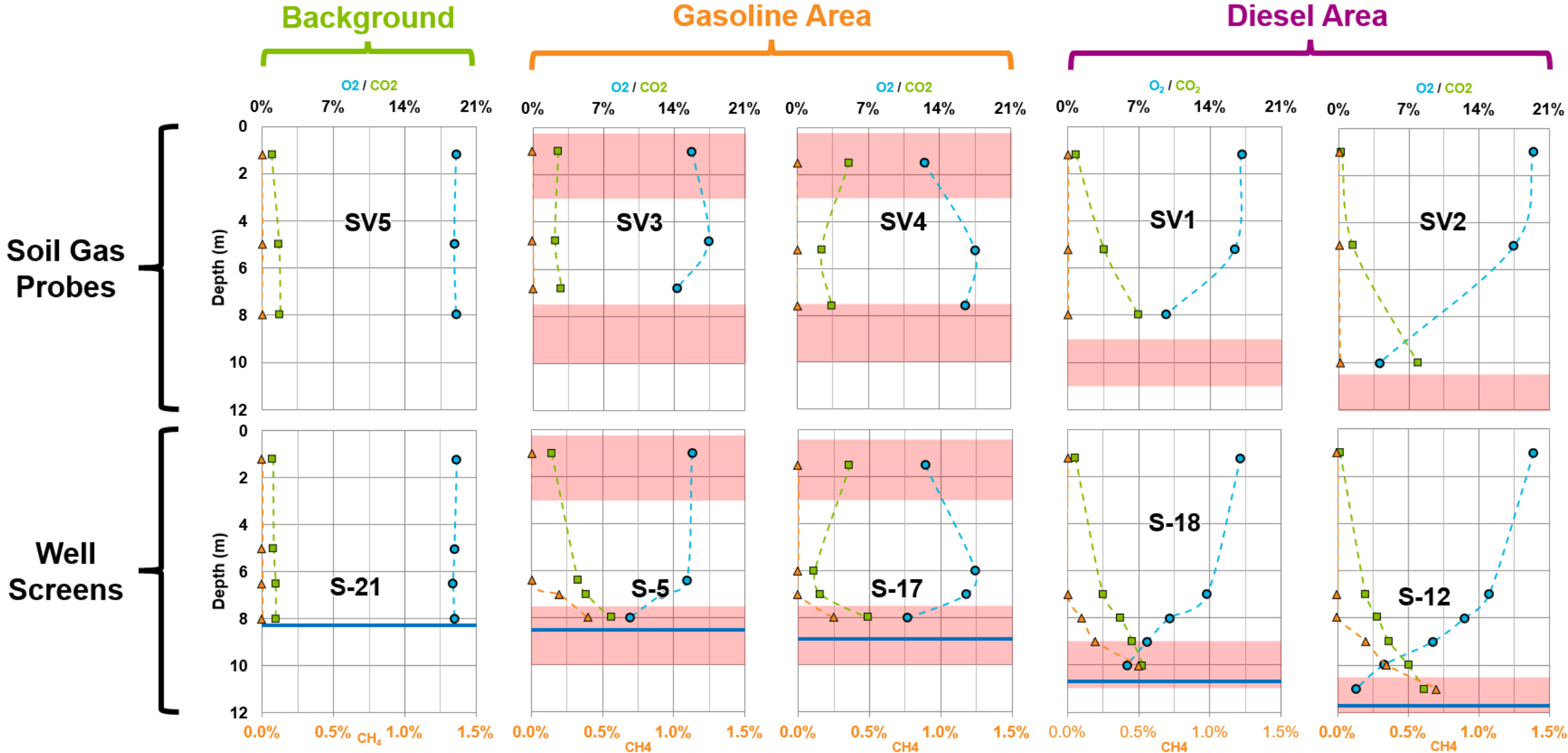
# Soil Gas Concentration Gradient Method (Quarterly)

- Field analysis of soil gas ( $O_2$ ,  $CO_2$ , and  $CH_4$ )
- Nested soil gas probes: 3 depths per location
- Profiling in wells: 1-meter intervals within screened interval





# Soil Gas Profiling – Soil Gas Probes vs Wells



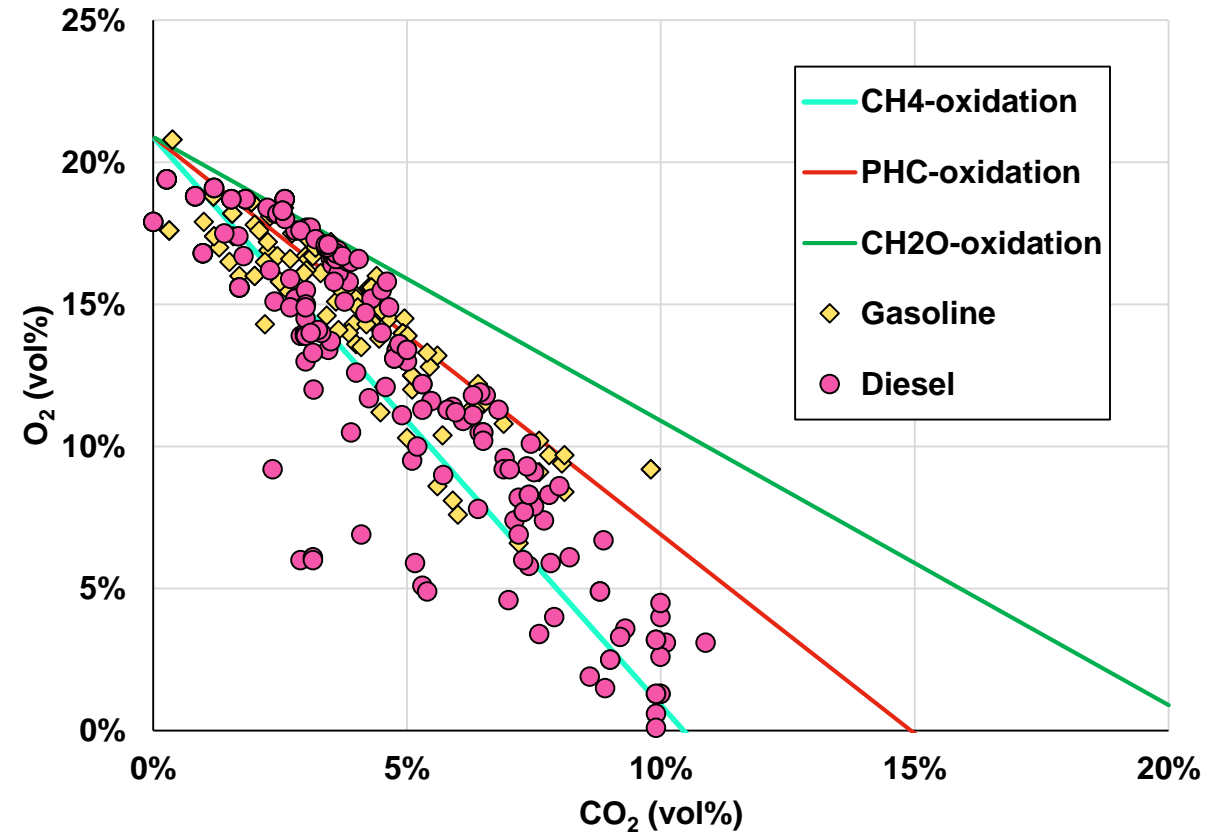
# Gradient Method Results

- NSZD Rates estimated from wells generally higher than soil gas probes
- Lower density of measurements near base of vadose zone with prescribed, fixed-depth probes

- O<sub>2</sub> gradients yield higher NSZD rates than CO<sub>2</sub> gradients, particularly in diesel area
- Possible CO<sub>2</sub> dissolution/reaction with soil matrix minerals (USEPA, 1995; Romanak et al., 2012)

Gasoline Area (L/ha/yr)				Diesel Area (L/ha/yr)			
SV3		SV4		SV2		SV1	
O <sub>2</sub>	CO <sub>2</sub>	O <sub>2</sub>	CO <sub>2</sub>	O <sub>2</sub>	CO <sub>2</sub>	O <sub>2</sub>	CO <sub>2</sub>
280	200	290	260	1300	830	930	680

Gasoline Area (L/ha/yr)											
S-5		S-6		S-10		S-15		S-16		S-17	
O <sub>2</sub>	CO <sub>2</sub>	O <sub>2</sub>	CO <sub>2</sub>	O <sub>2</sub>	CO <sub>2</sub>	O <sub>2</sub>	CO <sub>2</sub>	O <sub>2</sub>	CO <sub>2</sub>	O <sub>2</sub>	CO <sub>2</sub>
970	830	1600	1500	1100	680	440	380	1400	1100	1500	1200
Diesel Area (L/ha/yr)											
S-7		S-8		S-9		S-12		S-18		S-19	
O <sub>2</sub>	CO <sub>2</sub>	O <sub>2</sub>	CO <sub>2</sub>	O <sub>2</sub>	CO <sub>2</sub>	O <sub>2</sub>	CO <sub>2</sub>	O <sub>2</sub>	CO <sub>2</sub>	O <sub>2</sub>	CO <sub>2</sub>
820	580	2000	1300	1400	760	1100	820	1500	930	1100	670



# Biogenic Heat Method

- Temperature in 1-meter depth increments
- 13 months of continuous temperature measurements using data loggers
- Gasoline area (S-5)
- Diesel area (S-7)
- Background (S-21)
- Quarterly manual temperature measurements
- Wells instrumented with data loggers
- 15 additional wells in gasoline and diesel area



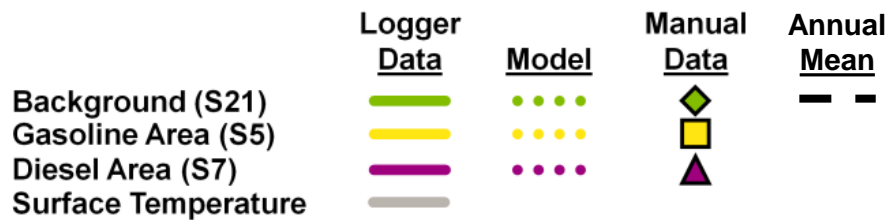
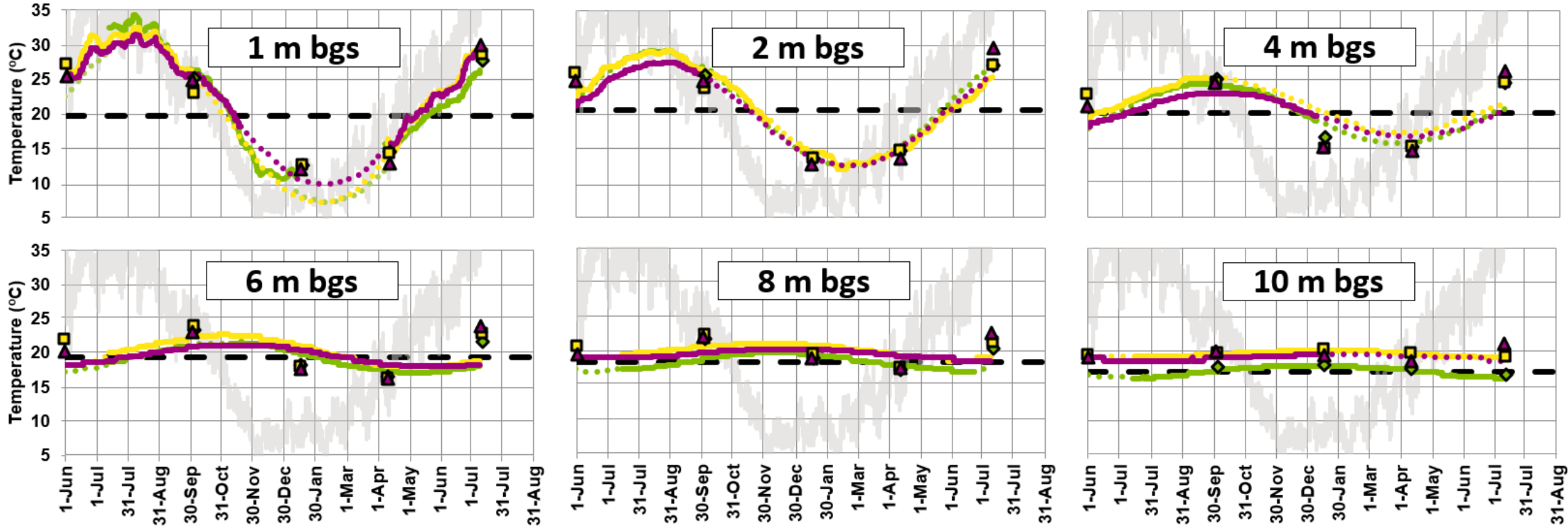
Temperature Data Loggers



Thermistor used for Manual Readings

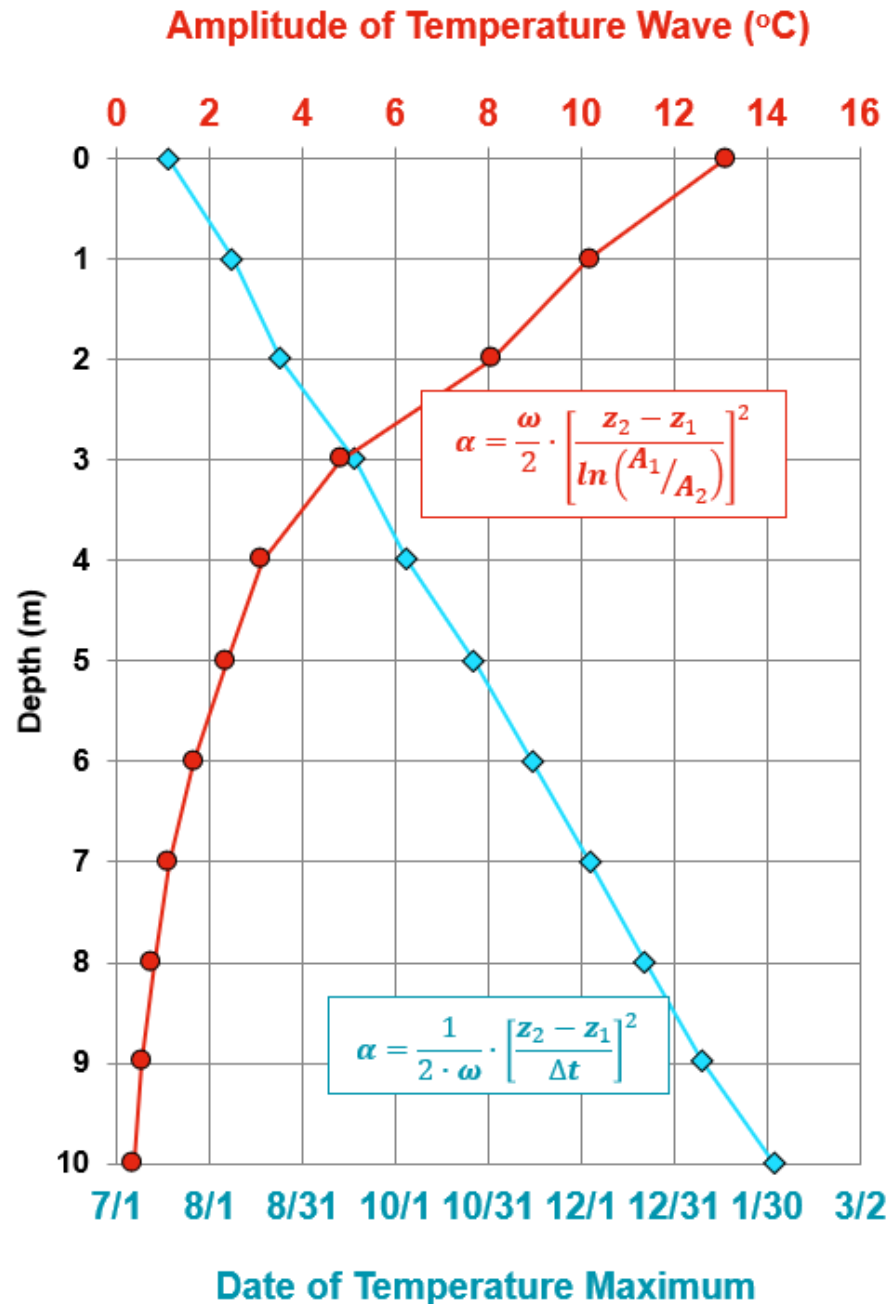
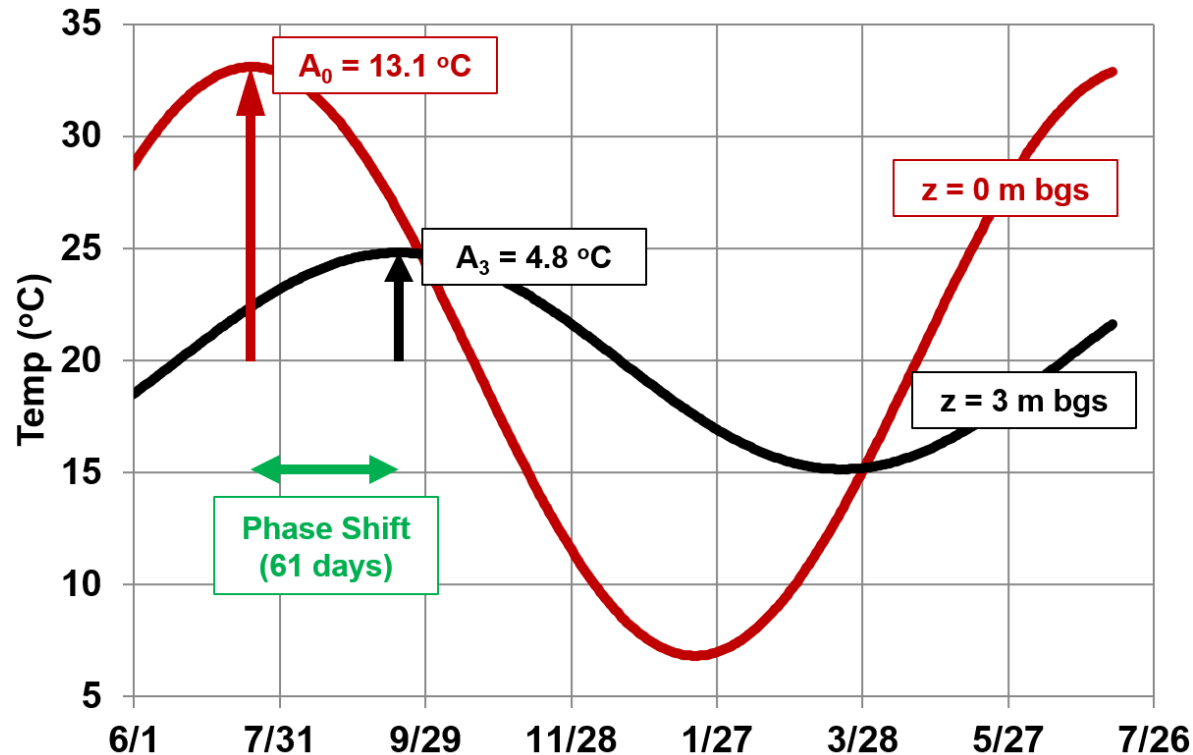


# Temperature Data



# Temperature Data Analysis

- Site-specific thermal diffusivity ( $\alpha$ ) estimated from data logger measurements
- Amplitude ratio and phase lag methods for 1<sup>st</sup> harmonic (Carson 1963; Sweeney and Ririe, 2014)
- Thermal conductivity estimated from diffusivity and heat capacity measurements.



Thermal Diffusivity ( $\alpha$ )  
10<sup>-6</sup> m<sup>2</sup>/sec

1.1

1.2

1.0

0.92

1.3

0.7

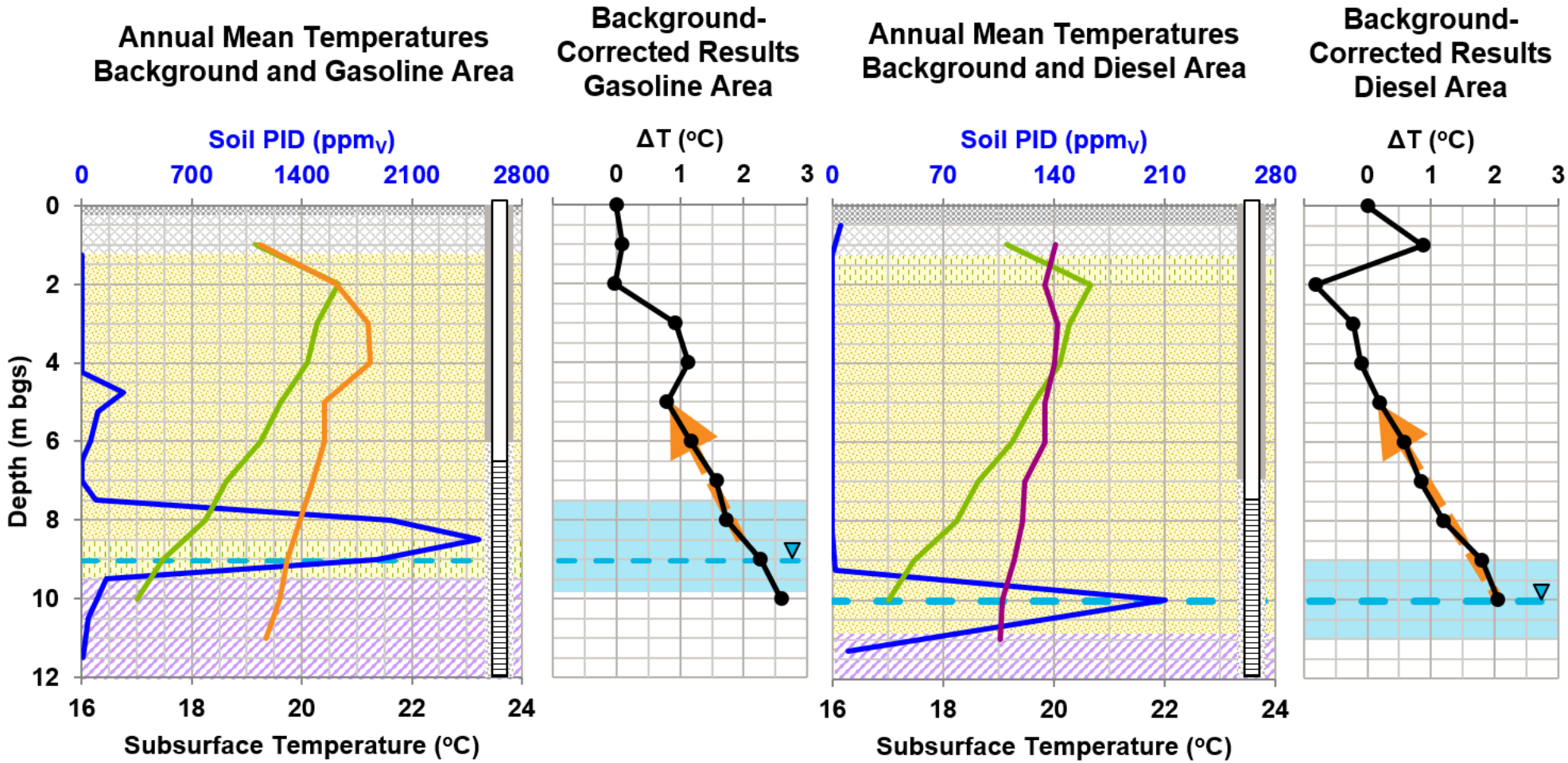
0.85

1.4

1.2

1.2

# Temperature Data Analysis – Data Loggers



**Annual Average Temperature Profile Results:**

- Gasoline Source Zone  
3,000 L/ha/yr
- Diesel Source Zone  
3,200 L/ha/yr

**LEGEND**

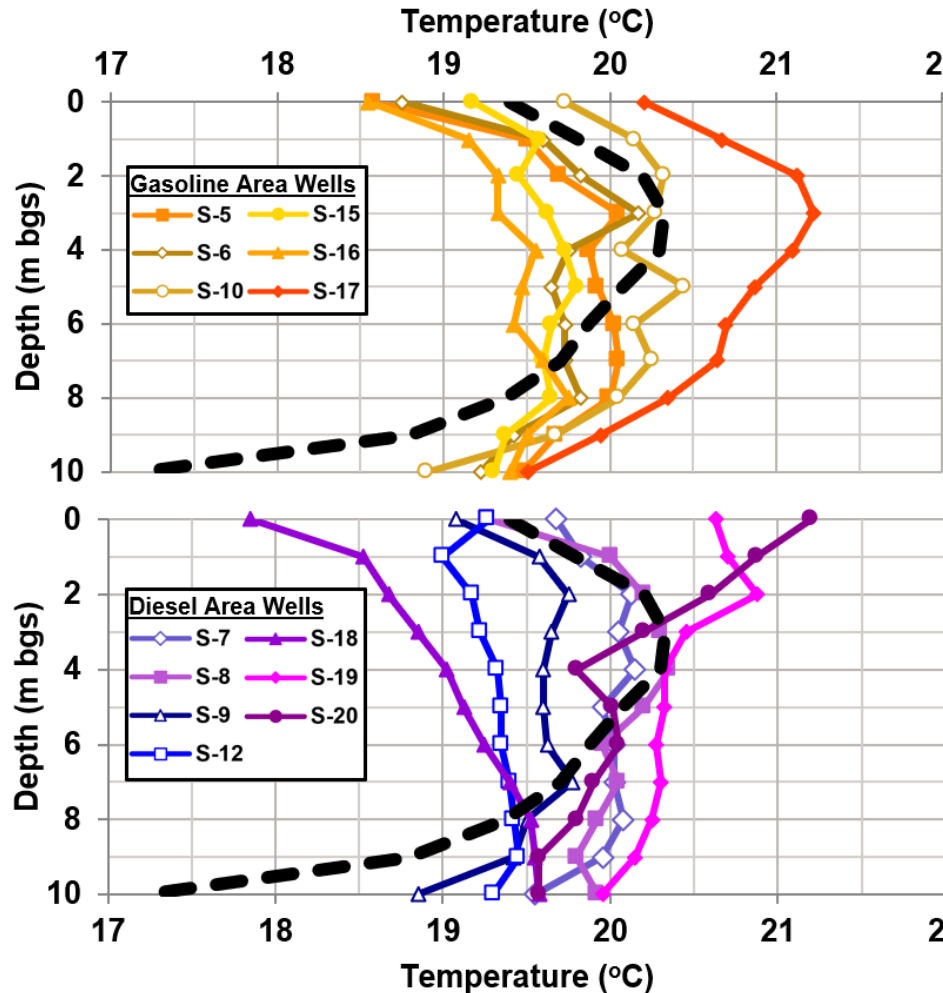
- Photoionization Detector Reading
- S-21 Temperature Profile (Background)
- S-5 Temperature Profile (Gasoline Area)
- S-7 Temperature Profile (Diesel Area)
- ▽ Average Depth to Water
- Range of Water Table Fluctuation

**GEOLOGY**

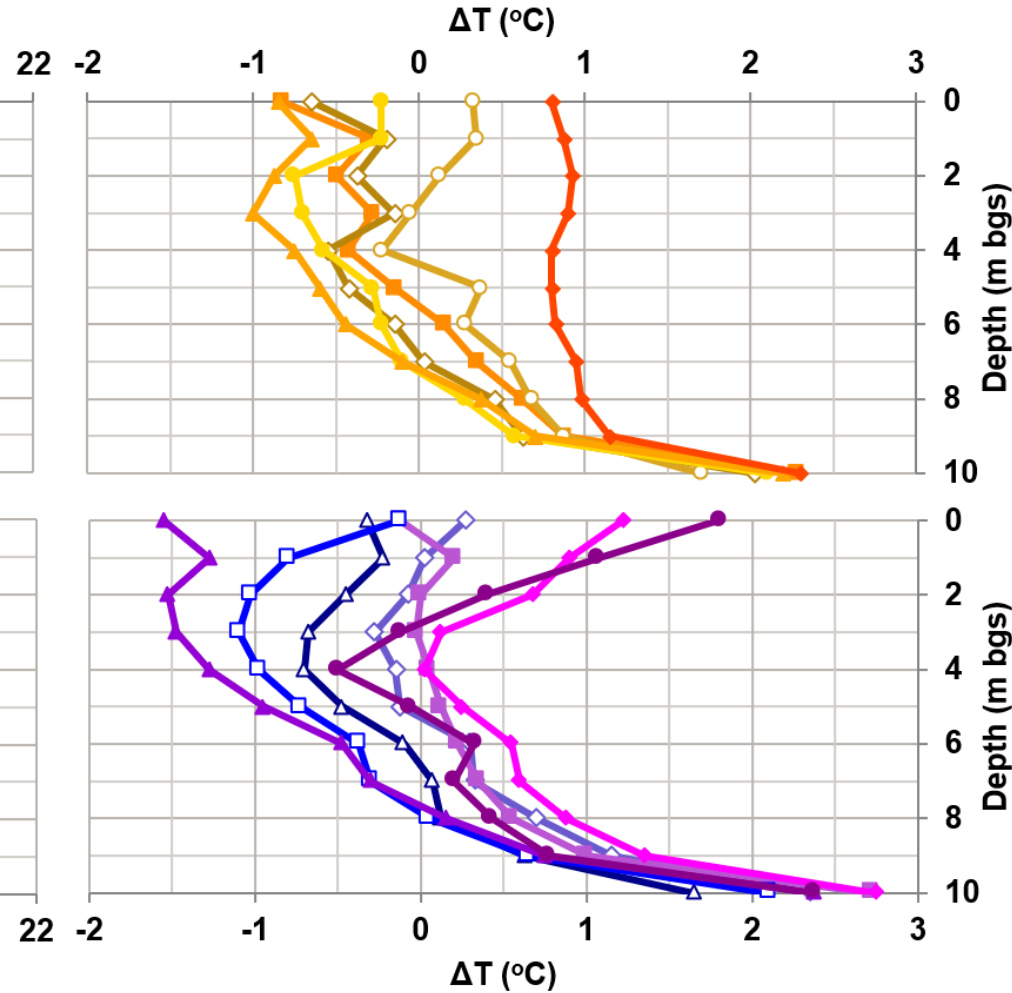
- ▨ Pavement
- ▨ Silty Sand
- ▨ Fill
- ▨ Clay
- ▨ Silt, Sand & Gravel

# Temperature Data Analysis – Manual Measurements

Average Temperatures from Quarterly Manual Measurements



Average Background-Corrected Temperatures from Quarterly Manual Measurements

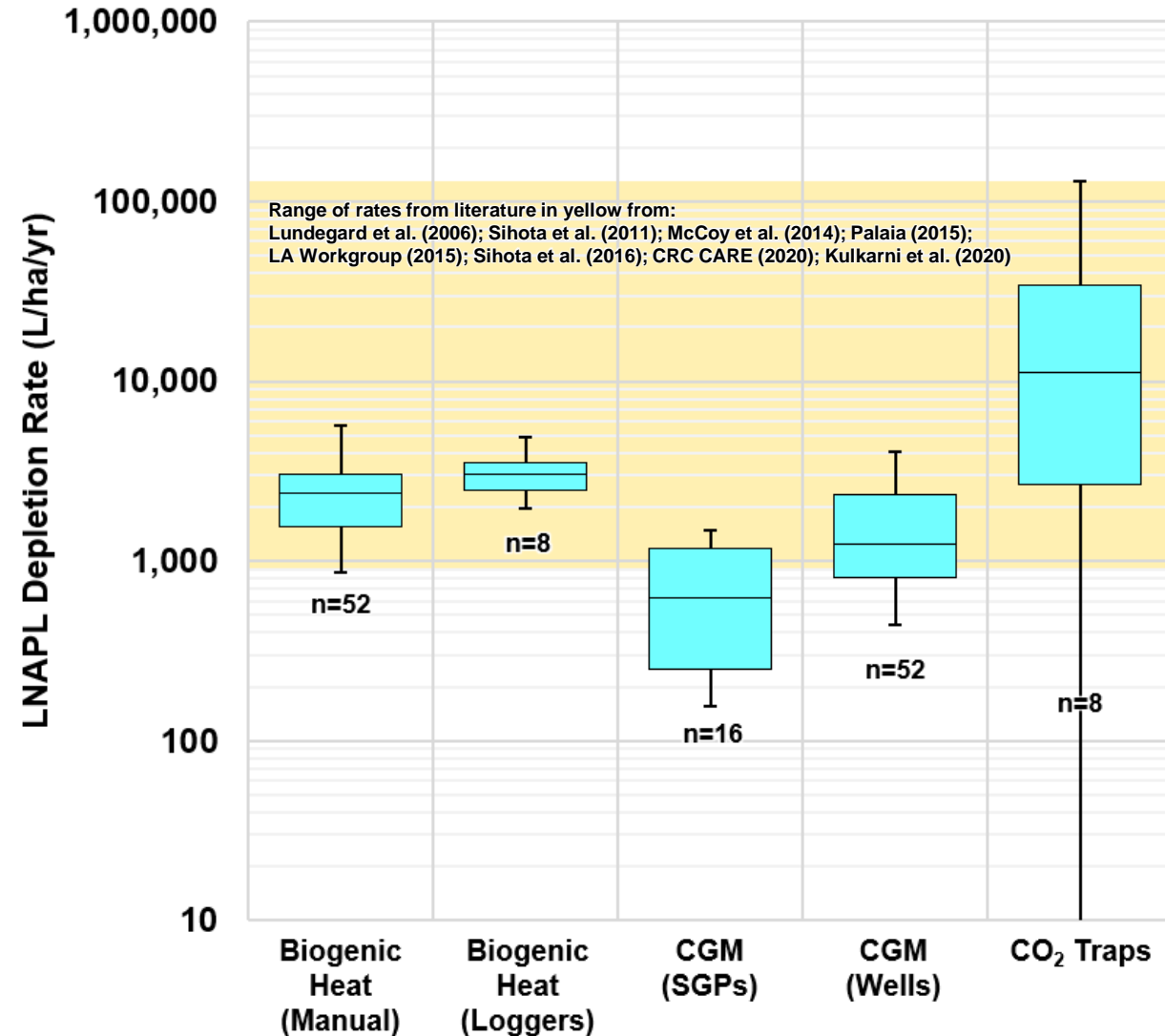


## Temperature Profile Results:

- Gasoline Source Zone  
2,000 – 2,700 L/ha/yr
- Diesel Source Zone  
1,900 – 3,200 L/ha/yr

# Study Results

- Large variability in rates, but all methods demonstrate NSZD
- CSM is key to interpreting data and identifying potential interferences
  - Lateral soil gas transport in upper 5 to 6 m
  - O<sub>2</sub> utilization and CO<sub>2</sub> production in multiple depth horizons
  - Possible consumption of CO<sub>2</sub> by dissolution and reaction with soil minerals
- Results highlight value of measurements of soil gas and temperature in existing wells
  - CSM testing and method screening
  - Can be qualitative or quantitative





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